

The Chemistry of Ruthenium in PSSA Ionomer: Reactions of Ru-PSSA with CO, H₂, O₂, and Alcohols

IL WUN SHIM, VINCENT D. MATTERA, JR.,¹ AND WILLIAM M. RISEN, JR.²

Department of Chemistry, Brown University, Providence, Rhode Island 02912

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Ru(III) ions have been incorporated in the domains of sulfonated linear polystyrene (PSSA) as a dispersion medium to form PSSA-Ru(III) films through an ion-exchange process. The chemical reactivities of PSSA-Ru(III) films have been investigated by reacting the ruthenium sites with CO, H₂, O₂, CH₃OH, and C₂H₅OH under mild conditions. The reactions of PSSA-Ru(III) films with CO (400 Torr) in the temperature range 25-186°C resulted in four different Ru carbonyl species, which were characterized by their infrared spectra. Treatment of PSSA-Ru(III) films with hydrogen (400 Torr) at 150°C produced ruthenium hydride species, which were confirmed by identifying the corresponding ruthenium deuterides. Also, H-D exchange on benzene rings of the polystyrene backbone was found to occur during the reaction of PSSA-Ru(III) films with D₂. The reactions of aqueous methanol and ethanol with PSSA-Ru(III) films produced ruthenium carbonyl species, but there was no evidence of the formation of ruthenium hydride or ruthenium formyl groups in the infrared spectra. Static Fischer-Tropsch type reactions of PSSA-Ru(III) powder with CO (300 Torr) and H₂ (300 Torr) at 150°C showed the formation of various aliphatic hydrocarbons, oxygen-containing hydrocarbon compounds, and CO₂ in the mass and infrared spectra. © 1985 Academic Press, Inc.

INTRODUCTION

Supported transition metals have been studied extensively as catalysts that can be operated under relatively mild conditions, and many reactions have been reported to be catalyzed by metals supported by such inorganic oxides as zeolites (1), alumina (2), and silica (3). Functionalized organic polymers also have been used as supports and are of particular interest for heterogenized homogeneous catalytic processes (4). In these cases transition metal-containing complexes that are either active catalysts or potential catalytic precursors usually are bound to the polymer support by covalent attachment (5). It is possible, of course, to use transition metals supported on ionic polymers as catalysts, and there have been reports of catalytic reactions in-

volving transition metal complexes incorporated into ion-exchange resins (6). While such resins are polyelectrolytic, they are not thought to possess the potentially useful morphological properties of ionomers.

Ionomers are polymers that are functionalized with ionic groups (usually anionic sites) attached at various points along the polymeric backbone. Such materials have a tendency to form ionic domains in which the anionic groups are microphase-separated from the typically hydrophobic backbone portions of the polymer (7, 8). As a result, ionic domains are formed that are largely surrounded by a medium of low dielectric constant formed by the network, although the domains may be connected to one another by channels. The ionic 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 (9), and can be

¹ Present address: AT&T Bell Laboratories, 600 Mountain Rd., Murray Hill, N.J.

² To whom correspondence should be addressed.

thought of as a small isolated chemical reactor.

If the metal ions in the domains 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. Such reactant molecules could be confined for a residence time that would permit the sites and reactant to interact much as they would if they were surface sites and gaseous reactants from a gas at much higher pressure. Moreover, the ionomers have other potential advantages. For example, the domain structure could control the size distribution of metal particles formed by reduction, contain protons adjacent to reduced metal species, confine intermediates for subsequent reactions, or serve other reaction control functions.

Ruthenium is well known to act catalytically in both homogeneous and heterogeneous reactions. Thus, ruthenium complexes raise methanol to its ethanol homolog in the presence of iodide promoters and H_2/CO . When acid-promoted, these catalysts are thought to contain Ru(II) carbonyl complexes such as $[Ru(CO)_3I_3]^-$, $Ru(CO)_4I_2$, or $[Ru(CO)_3I_2]_2$. Synthesis of ethanol also is thought to proceed directly from H_2/CO , through the initial formation of an $H-M-CO$ species (10). While this forward reaction is of obvious practical importance, it also is feasible for the reverse process, decomposition of ethanol to a ruthenium carbonyl hydride, to proceed. The decomposition of methanol and of ethanol, introduced into Ru-containing domains of sulfonated polystyrene (PSSA)-supported ruthenium, may be expected to lead to PSSA-Ru carbonyl and hydride species by analogy to the solution and solid-support catalyzed reactions.

Heterogeneous reactions of Ru on oxide supports also are well known. For example,

in their study of CO chemisorption on silica-supported Ru, Brown and Gonzalez (11) found that CO is adsorbed on reduced Ru sites, at which it has a stretching frequency of 2030 cm^{-1} , and on oxidized Ru sites, at which it gives rise to $\nu(CO)$ bands at 2080 and 2135 cm^{-1} . Similarly, Dalla Betta (12) studied the infrared spectra of CO adsorbed on alumina-supported Ru of varying metal particle sizes. He found one $\nu(CO)$ band when the particles were about 100 \AA in diameter, but three such bands when they had diameters of less than 60 \AA .

Recently, Bell *et al.* (13) studied the infrared spectra of supported ruthenium cluster organometallic compounds. Decomposition of the supported clusters reportedly gave rise to three types of species independently of the original cluster composition. For example, the infrared spectra of silica-supported $Ru_3(CO)_{12}$ that had been reduced by H_2 at 350°C and then exposed to CO contained bands at 2139, 2063, and 2039 cm^{-1} . It is interesting to note that under each of these types of conditions, when either reduced supported Ru cations or decomposed supported Ru clusters are exposed to H_2 , ruthenium hydrides generally are not observed when the support is an inorganic oxide.

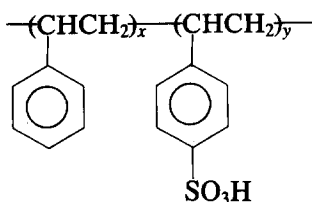
Recently, we have reported (15) results of a study involving the reactions of small gaseous molecules with rhodium contained within the ionic domains of sulfonated polystyrene (PSSA) ionomers.

Given the importance of the reactions of supported Ru with CO and H_2 , the role of Ru in methanol and ethanol chemistry, and the potentially interesting morphological consequences of using an ionomer support, we have carried out reactions of Ru in the domains of sulfonated polystyrene ionomer. The results are reported in this paper.

EXPERIMENTAL

The sulfonated linear polystyrene (PSSA) employed in this work was kindly provided by Dr. R. D. Lundberg and co-workers at Exxon Research and Engineer-

ing Company. Its chemical composition can be represented as follows:



Here, $y/(x + y)$ represents the mole fraction of sulfonate groups. The ionomer used has an average sulfonate composition of 16.7 mol%. Its preparation has been described by Lundberg and co-workers (14). Transparent thin films of this PSSA material were prepared at ca. 20 μm thickness, which is convenient for study by transmission infrared spectroscopy, by dissolving the H^+ form of PSSA in tetrahydrofuran (THF) and then allowing the solvent to evaporate at 25°C. In order to remove the solvent completely, the films were dried at 110°C under vacuum (ca. 1×10^{-2} Torr) for 1 day. The Ru(III) ions were incorporated by an ion-exchange process in which the PSSA films were stirred in (0.04 M) aqueous solution of $\text{RuCl}_3 \cdot 1-3\text{H}_2\text{O}$ (Alfa Products) at 25°C for 14 days. The dark brown colored films resulting from the ion-exchange reaction were rinsed thoroughly with distilled water, and dried at 110°C under vacuum for 2 days. The films are designated in the form PSSA-Ru(A)B where A gives the oxidation state of ruthenium and B designates the other chemical constituents.

The Ru-exchanged films were analyzed by the Schwarzkopf Microanalytical Laboratory and shown to contain an average 3.44% Ru (calcd 4.57%), 4.39% S (calcd 4.34%), and a trace of Cl (less than 0.09%). The calculated percentages were obtained by assuming that each Ru cation carries a +3 charge and neutralizes three sulfonate groups, as described under Results and Discussion.

For the methanol decomposition reactions, the PSSA-Ru films were stirred in 25 vol% aqueous methanol ($\text{CH}_3\text{OH}/\text{H}_2\text{O}$,

$^{13}\text{CH}_3\text{OH}/\text{H}_2\text{O}$, or $\text{CD}_3\text{OD}/\text{D}_2\text{O}$) for 3 h then dried in air at room temperature prior to loading them into the reactor.

Some PSSA-Ru films were prepared by ion-exchanging 16.7 mol% sulfonated H-PSSA films with $\text{RuCl}_3 \cdot 1-3\text{H}_2\text{O}$ in 14 vol% aqueous ethanol solution. The films acquired a dark brown-black color within 7 days and the degree of ion exchange was determined spectroscopically. While the exchange was about 75% complete with aqueous solutions, it was found to be nearly 100% complete for these films. This also is consistent with the elemental analysis when allowance is made for the presence of approximately 10 wt% solvent ($\text{C}_2\text{H}_5\text{OH}/\text{H}_2\text{O}$). Thus, the analysis for Ru and S, compared to calculated values for solvent-free PSSA-Ru, gave 4.00% S (calcd 4.34%) and 4.08% Ru (calcd 4.57%). In addition, electron microprobe analysis on these films, recorded on a EDAX Model 711 interfaced to an AMR 1000 SEM, showed only a trace of Cl in addition to the strong peaks that represent Ru and S.

The gases used in this work, carbon monoxide (99.99% CO, Matheson Corp.), isotopic carbon monoxide (99% ^{13}C O, Monsanto Research), hydrogen (99.995% H_2 , Airco, Inc.), deuterium (99.995% D_2 , Matheson Corp.), and oxygen (99.5% O_2 , Airco, Inc.) were purified further by passing the gases through liquid-nitrogen traps, or acetone/dry-ice traps, upon their addition to the reactor.

For the reactions of Ru-exchanged PSSA films with small gaseous molecules, a specially designed reactor/infrared cell was used (15). It has a Pyrex body, with KBr windows affixed using a cyanoacrylate glue, and can be connected conveniently to a vacuum line or gas supply line. Using this cell, infrared spectra were taken *in situ* of films subjected to various treatments. The geometric center of the 1.5-cm-diameter circular PSSA films 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 using an external magnet. There are no metal surfaces in the system. The reactor was heated by using external heating tape and the temperature was monitored with a Chromel–Alumel thermocouple which was located to sense the reactor temperature through the cell wall. The PSSA–Ru films were treated with gases in this reactor under the conditions described under Results and Discussion.

The infrared spectra in the region 3800–400 cm^{-1} were recorded on Digilab FTS-15B FT-IR spectrometer with 2- cm^{-1} resolution. A Phillips Model 201 transmission electron microscope operated at 100 kV in the bright-field mode was used to investigate the PSSA–Ru films after reduction reactions with H_2 , as described under Results and Discussion. These samples were prepared by embedding the films in Spurr's low-viscosity medium and microtoming them into sections which were supported on Cu grids.

The gaseous products from the reaction of static Fischer–Tropsch reaction were investigated using a Perkin–Elmer 397 mass spectrometer.

RESULTS AND DISCUSSION

The PSSA–Ru films were characterized and then reacted with CO , H_2 , O_2 , CH_3OH , $\text{C}_2\text{H}_5\text{OH}$, and several isotopic analogs in various combinations under a range of conditions. The results are presented and discussed in the following section. The spectral features associated with the species identified are summarized in the last figure.

Ion-Exchange Formation of Ru–PSSA Films

The effectiveness of the ion exchange of PSSA films with Ru(III) ions was evaluated by both elemental analysis and infrared spectroscopy. The ruthenium-exchanged PSSA films contained an average of 3.44 wt% of ruthenium. If the exchanged Ru(III) species has a +3 charge, which is likely

given the acidic environment, and can effect complete ion exchange, 4.57 wt% Ru would be calculated for the dry ionomer. Only a trace of chlorine was found in the sample, so Ru is not present as a chloro species. Thus, the elemental analysis means that approximately 75% of the sulfonic acid groups are exchanged by Ru(III) ions. This may be due to physical constraints on the access of SO_3^- groups to the Ru(III), due to domain formation, or to chemistry involving partial hydrolysis of the species, but in any event the stoichiometry is equivalent to having 75% of the SO_3^- units coordinated to a Ru(III) species and 25% to H^+ .

The infrared spectra of PSSA–Ru(III) films exhibit three strong bands at 1029, 1124, and 1280 cm^{-1} , which are due to characteristic stretching vibrations of SO_3^- groups, as well as many bands due to the polystyrene backbone. These three bands are readily assigned, and may be compared, for example, to the bands at 1036, 1146, and 1273 cm^{-1} observed in the infrared spectrum of Fe(III)-exchanged crosslinked sulfonated polystyrene films by Zundel (16), who concluded that three sulfonate groups interact with each Fe(III) ion. From the infrared spectra, which include bands at 2950 (s.sh) and 2405 (m.br) cm^{-1} that are characteristic of $-\text{SO}_3\text{H}$ groups, the electrical charge balance between the sulfonate group and Ru(III) ion, and the elemental analysis, we conclude that most of the Ru(III) ions in the PSSA films interact with three SO_3^- groups and that the remaining SO_3^- groups are protonated.

Reaction of CO with PSSA–Ru(III) Films

A number of infrared studies of CO adsorbed on ruthenium supported by Al_2O_3 (12, 13), SiO_2 (11, 13, 17, 18), and MgO (19) have been carried out to understand the important catalytic properties of Ru. The reported infrared spectra of such Ru carbonyl species consistently show bands in three regions (20): 2125–2160 cm^{-1} , 2060–2086 cm^{-1} , and 2020–2050 cm^{-1} . Typ-

ically, the low-frequency bands (2020–2050 cm^{-1}) have been assigned to CO that is linearly adsorbed on reduced Ru; the bands in the region 2060–2086 cm^{-1} to CO adsorbed on oxidized Ru; and, the high-frequency bands (2125–2160 cm^{-1}) to CO adsorbed on a ruthenium oxide or physically adsorbed CO on surface ruthenium oxide. These facts constitute a useful starting point to consider the following experimental results.

In the first set of experiments, CO was added to dehydrated PSSA–Ru(III) films in the reactor cell at 400 Torr (1 Torr = 133.3 N m^{-2}) and 150°C. After 18 h the reactor was evacuated (to $P \cong 1 \times 10^{-2}$ Torr) at room temperature. In the resulting infrared spectrum, five new strong $\nu(\text{CO})$ bands were found at 2150, 2085, 2067 (sh), 2020, and 1985 cm^{-1} . These features are shown in Fig. 1b along with the spectrum of the un-

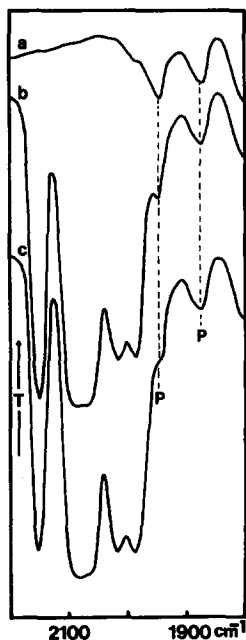


FIG. 1. IR spectra of CO adsorption and desorption in [PSSA–Ru(III)] film; (a) [PSSA–Ru(III)] film; (b) CO adsorption (400 Torr) at 150°C for 18 h followed by evacuation of the CO from the reactor at 25°C for 20 min; (c) CO desorption reaction from (b) at 150°C for 12 h under vacuum (10^{-2} Torr). On this and succeeding figures, bands marked P are due to the polymer substrate.

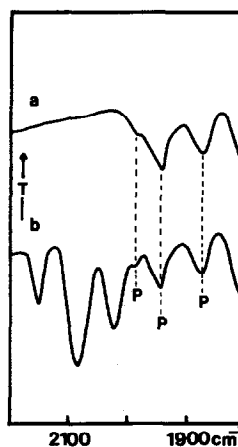


FIG. 2. IR spectra of CO adsorption in [PSSA–Ru(III)] film after oxidation by O_2 . (a) [PSSA–Ru(III)] film after exposing O_2 (400 Torr) at 150°C for 60 h; (b) CO adsorption (400 Torr) at 144°C for 9 h.

reacted PSSA–Ru(III) film in Fig. 1a. When the reactor cell was evacuated at 150°C and 1×10^{-2} Torr for 12 h, it was found that these band intensities decreased by about 10%, as shown in Fig. 1c.

At this stage, the bands due to the CO adsorption on and/or reactions with PSSA–Ru(III) films could not be interpreted solely by comparison with infrared data reported for other Ru carbonyl species. In an attempt to investigate the nature of these Ru carbonyl species further, the PSSA–Ru(III) films were treated with CO under a variety of conditions, including treatment with oxidizing or reducing reagents before and after CO addition and variation of reaction temperature and CO pressure.

When PSSA–Ru(III) films were treated first with O_2 (400 Torr) at 150°C and then exposed to CO (400 Torr) at 144°C for 9 h, three bands were found in the $\nu(\text{CO})$ region at 2151, 2087, and 2022 cm^{-1} (Fig. 2b). This result, in comparison to the spectrum from the reaction of PSSA–Ru(III) with CO shown in Fig. 1, indicates that the Ru(III) dispersed in the PSSA film was not oxidized under these conditions to form higher-oxidation-state ruthenium species such as ruthenium oxide. Therefore, these three bands are due to some Ru(III) car-

bonyl species, or to physically adsorbed CO.

Reactions of PSSA–Ru(III) with CO, as a function of CO pressure, reveal that the aforementioned three bands have two different origins. As illustrated in Fig. 3, the bands at 2085 and 2020 cm^{-1} appear at the same time, prior to the appearance of the band at 2150 cm^{-1} , and become more intense as the CO pressure increases. A weak new band at 2150 cm^{-1} appears when the pressure of CO is increased to 200 Torr, and its intensity increases slightly with further increase of CO pressure. The intensities of these three $\nu(\text{CO})$ bands do not change further when the pressure of CO is increased to 400 Torr at constant temperature (100°C). Thus, upon comparing the infrared spectra shown in Figs. 2 and 3 as well as known Ru carbonyl species, we assign the bands at 2085 and 2020 cm^{-1} to PSSA–Ru(III)(CO)₂. The band at 2150 cm^{-1} is tentatively assigned to physically adsorbed CO, since it appeared at higher pressure than the other two $\nu(\text{CO})$ bands at

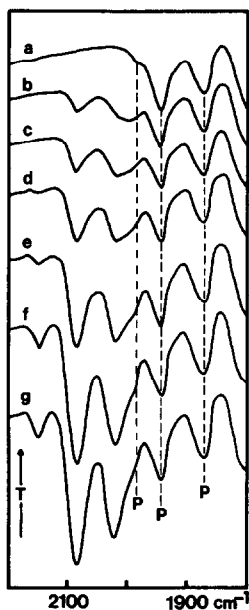


FIG. 3. IR spectra of CO adsorption as a function of CO pressure at 100°C. (a) [PSSA–Ru(III)] film; (b) CO, 60 Torr, for 1 h; (c) 120 Torr, 1.5 h; (d) 200 Torr, 2 h; (e) 300 Torr, 2 h; (f) 400 Torr, 17 h; (g) 500 Torr, 28 h.

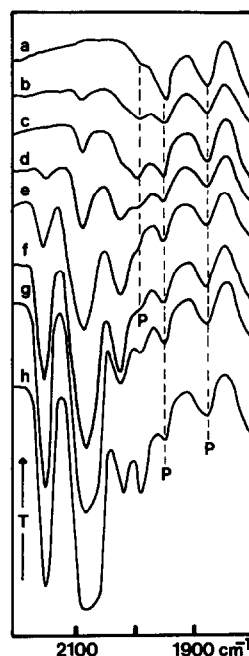
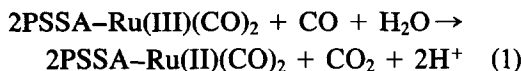


FIG. 4. IR spectra of CO adsorption (400 Torr) as a function of temperature. (a) [PSSA–Ru(III)] film; (b) 25°C, 12 h; (c) 50°C, 7 h; (d) 70°C, 10 h; (e) 100°C, 24 h; (f) 130°C, 20 h; (g) 160°C, 20 h; (h) 186°C, 40 h.

2085 and 2020 cm^{-1} , disappeared upon reaction with H₂, or O₂, and decreased upon desorption at 150°C under vacuum for 12 h (see Figs. 1b and c).

As expected, the interaction between PSSA–Ru(III) films and CO varies with reaction time and temperature. For relatively short reaction times and low temperatures, the development of bands in the $\nu(\text{CO})$ region occurs much as was shown in Fig. 3. However, as seen in Fig. 4, once the reaction temperature is increased to over 100°C with constant CO pressure (400 Torr), changes begin to be observed. At reaction temperatures in the range 130–186°C, the band at 2085 cm^{-1} becomes broader and a shoulder develops at 2067 cm^{-1} while a band at 1985 cm^{-1} becomes stronger and more distinct. These two bands at 2067 and 1985 cm^{-1} come from another Ru carbonyl species that is formed at higher reaction temperature. We postulate that Ru(III) ions in PSSA ionomer are reduced to Ru(II) in

the presence of CO and H₂O by the following overall reaction:



This postulate is based on the analogous reduction of Ru(III) to Ru(II) by CO in solution. Other analogous reactions have been postulated to occur in the case of PSSA-Rh (15) and zeolite-supported rhodium under similar conditions (21). Thus, the two bands at 2067 and 1985 cm⁻¹ are assigned to the dicarbonyl, PSSA-Ru(II)(CO)₂.

While $\nu(\text{CO})$ bands have thus been assigned to adsorbed CO in Ru(III) and Ru(II) species, there also is the possibility that Ru(0) species can be formed in the PSSA-Ru ionomer by a reduction involving the CO/H₂O (water gas shift) reaction. It is well known that Ru(0) species can be formed on inorganic oxide supports by reduction with hydrogen at temperatures above 300°C. In order to discover whether Ru(0) species can be formed in the PSSA-Ru ionomer, and, indeed, under mild conditions, the PSSA-Ru(III,II)(CO)₂ films of the type resulting from the previous reaction were treated with hydrogen (400 Torr) at 186°C for 20 h. When this reaction was carried out, three new bands appeared at 2050, 2001, and 1968 cm⁻¹, with shoulders at 2085 and 2067 cm⁻¹, while the band at 2150 cm⁻¹ disappeared completely, as shown in Fig. 5b.

These three new bands are quite similar to the $\nu(\text{CO})$ bands observed in the infrared spectra reported by Bell *et al.* (13) in the study of alumina-supported ruthenium cluster carbonyls, in which the three $\nu(\text{CO})$ bands appeared when Ru₃(CO)₁₂, H₄Ru₄(CO)₁₂, and Ru₆C(CO)₁₇ adsorbed on γ -Al₂O₃ and SiO₂ were thermally decomposed and subsequently exposed to CO after reduction reaction with hydrogen at 300–400°C. Several of the bands are close to those reported by Guglielminotti *et al.* (22) ($\nu(\text{CO})$: 2054, 1977 cm⁻¹) for a species pos-

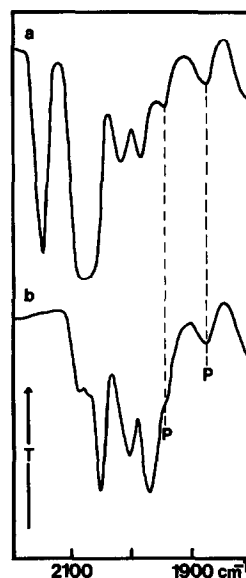


FIG. 5. IR spectra from the reduction reaction by H₂ of chemisorbed CO. (a) CO adsorbed on [PSSA-Ru(III)] film (400 Torr CO, 186°C, 40 h) and (b) after reduction reaction by H₂ (400 Torr) at 186°C, 20 h.

tulated as Ru(0)(CO)₂ that resulted when Ru₃(CO)₁₂ on Al₂O₃ was decarbonylated at 150°C. Another species postulated as a Ru(0) carbonyl, specifically Ru(0)(CO)₄, was reported by Liu *et al.* (23) in the study of surface-confined mononuclear and trinuclear ruthenium(0) carbonyl/phosphine complexes. It has three $\nu(\text{CO})$ bands at 2059, 1995, and 1952 cm⁻¹. Since the species formed upon reaction of partially reduced PSSA-Ru carbonyls with H₂ gives rise to bands at 2050, 2001, and 1968 cm⁻¹ that are quite similar to those known Ru(0) carbonyls, we postulate the formation of PSSA-Ru(0)(CO)_n ($n = 1-4$ species). Note that the Ru(0) species are not formed by reaction (1) with CO and H₂O at temperatures of up to 186°C, but they are formed when they are treated subsequently with hydrogen under the relatively mild conditions of 400 Torr H₂ and 186°C. The fact that two weak shoulders at 2085 and 2067 cm⁻¹ persist indicates that the treatment of the PSSA-supported ruthenium carbonyls with H₂ under these conditions does not effect complete reduction of Ru(III) or Ru(II)

to Ru(0). While these assignments to Ru(0) carbonyls are reasonable, the possibility that they result from hydride formation remained.

Adsorption of H_2 and D_2 on PSSA-Ru(III) Film

Despite extensive research on the reactions of ruthenium on inorganic oxide supports, there has been no report of the direct observation of ruthenium hydride species even though ruthenium hydrides are believed to exist as intermediates and to play an important role in various catalytic reactions. In the case of rhodium, however, Schwartz *et al.* (24) reported observing a rhodium(III) dihydride species on a silica support. It was discovered by treating silica-supported bis(allyl)rhodium with H_2 (1 atm). This rhodium hydride species was found to have high catalytic activity for olefin hydrogenation. The infrared spectral evidence for the rhodium hydride, which has two $\nu(\text{Rh-H})$ bands at 2080 and 2003 cm^{-1} , was confirmed by identifying two corresponding $\nu(\text{Rh-D})$ bands at 1450 and 1408 cm^{-1} . This discovery of rhodium hydrides on a silica support suggested the possibility of forming ruthenium hydride species in the PSSA-Ru films.

The treatment of PSSA-Ru(III) films with hydrogen (400 Torr) at 150°C for 7 days lead to the observation of four bands at 2065 (w), 2047 (w, sh) 1960 (m, sh), and 1945 (m) cm^{-1} , as shown in Fig. 6. We assign them to ruthenium hydride species. It is interesting to note that in the electron micrographs of such PSSA-Ru films, no metal clusters larger than 10 Å in diameter were observed.

In order to confirm the assignment to $\nu(\text{Ru-H})$ modes, freshly made PSSA-Ru(III) films were exposed to D_2 (400 Torr) at 150°C for 2 days, and four new bands were observed at 1475, 1469, 1402, and 1394 cm^{-1} . Among them, three bands at 1469, 1402, and 1394 cm^{-1} are assigned to Ru-D species. Treatment of an H-PSSA film with D_2 under the same conditions pro-

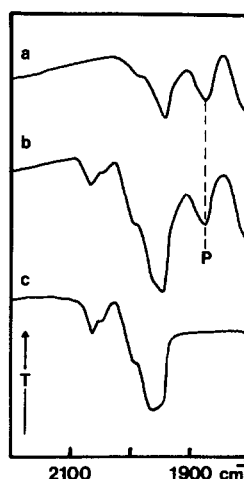


FIG. 6. IR spectra from the reaction of [PSSA-Ru(III)] film with H_2 . (a) [PSSA-Ru(III)] film; (b) after reaction with H_2 (400 Torr), 150°C, 7 days; (c) subtraction of spectrum (a) from spectrum (b).

duced a band at 1475 cm^{-1} (see Figs. 7b and c), so this band is not due to $\nu(\text{Ru-D})$. It is believed to come from vibrations of partially deuterated benzene rings. The three $\nu(\text{Ru-D})$ bands correspond to the isotopically shifted $\nu(\text{Rh-H})$ bands at 2065, 1960, and 1945 cm^{-1} , respectively. A band should appear also at around 1450 cm^{-1} to correspond to the $\nu(\text{Ru-H})$ band at 2047 cm^{-1} , but this region is masked by the skeletal stretching vibration band of benzene rings at 1453 cm^{-1} . The 1453- cm^{-1} band did become broader after treatment with D_2 , so this may indicate some underlying intensity due to this $\nu(\text{Ru-D})$. We conclude that ruthenium hydrides are produced in PSSA-Ru(III) films by reaction with H_2 under mild conditions. At this stage it is not clear whether the hydride bands are due to Ru multihydrides or from different Ru-H species at different ruthenium oxidation states.

In addition to the 1475- cm^{-1} band mentioned above, there is further evidence of H-D exchange on the benzene rings of the polystyrene backbone. As shown in Fig. 7, a strong band at 2266 cm^{-1} is observed after treatment of PSSA-Ru(III) with D_2 . This is due to a C-D stretching mode of deuterated benzene rings (15). There also are new

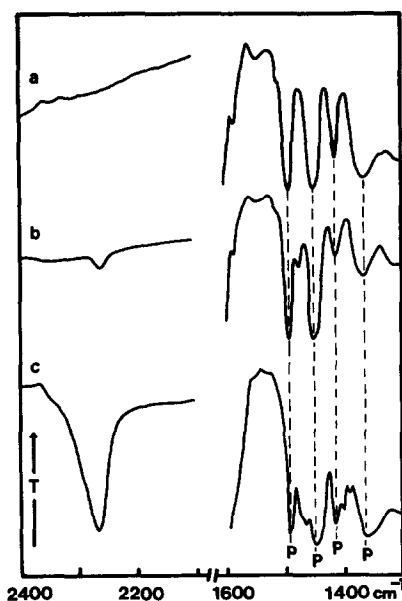


FIG. 7. IR spectra from the reaction of [PSSA-Ru(III)] film with D_2 . (a) [PSSA-Ru(III)] film; (b) spectrum of PSSA film without Ru after exposing to D_2 (400 Torr) at $150^\circ C$ for 48 h; (c) spectrum of [PSSA-Ru(III)] film after exposing to D_2 (400 Torr) at $150^\circ C$ for 48 h.

bands due to the in-plane bending (866 , 856 , 839 , and 809 cm^{-1}) and out-of-plane bending vibrations (732 and 684 cm^{-1}) of such rings. The treatment of H-PSSA films with D_2 under the same conditions also results in H-D exchange of benzene rings (see Fig. 7b), but the intensity of the band at 2266 cm^{-1} was quite weak compared to that shown in Fig. 7c. Consequently, it is believed that the H-D exchange of benzene rings (25) of the PSSA support involves Ru sites.

Methanol and Ethanol Decomposition Reactions in PSSA-Ru(III)

It is well known that alcohols such as ethanol and methanol decompose on metal surfaces to form such products as formaldehyde, carbon dioxide, and methylformate (26). Recently, however, a catalytic process for converting methanol or ethanol to hydrocarbons on a synthetic zeolite (ZSM-5) was developed and studied by workers at Mobil (27) and other groups (28, 29). In ad-

dition, Dombek and Warren reported in 1983 the formation of ethanol from H_2 and CO via homogeneous ruthenium catalysis, and inferred from the data that much of the ethanol might be derived from initially formed methanol (10).

In order to contribute to the understanding of the reaction chemistry of PSSA-supported ruthenium with alcohols, several reactions were carried out. In one type, dried PSSA-Ru(III) films were treated with 25% aqueous $^{12}CH_3OH$ at room temperature, and then heated at $150^\circ C$ under vacuum. The spectrum shown in Fig. 8b illustrates that methanol is decomposed in the PSSA-Ru(III) film and gives rise to four $\nu(CO)$ bands at 2081 , 2055 (vw, sh), 2101 (sh), and 1974 cm^{-1} . Then, other PSSA-Ru(III) films were treated with $^{13}CH_3OH$ under similar

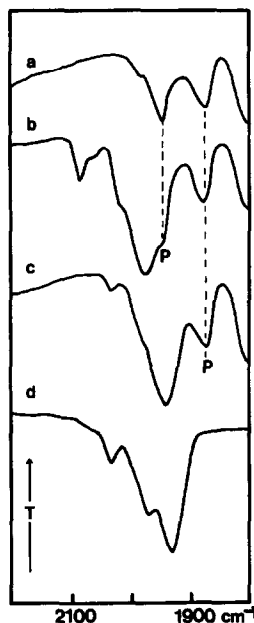


FIG. 8. IR spectra from the methanol decompositions on [PSSA-Ru(III)] film. (a) [PSSA-Ru(III)] film; (b) spectrum of [PSSA-Ru(III)] which was reacted with 25% aqueous CH_3OH , dried under vacuum at $25^\circ C$, and heated under vacuum at $150^\circ C$ for 5 days, spectrum was taken after evacuation for 30 min at $25^\circ C$; (c) spectrum of [PSSA-Ru(III)] after treating with 25% aqueous $^{13}CH_3OH$ and treating at $150^\circ C$ for 12 h under vacuum; (d) subtraction of spectrum (a) from spectrum (c).

conditions. As shown in Figs. 8c and d, the bands formed with CH₃OH are replaced by bands at 2033, 1970, and 1930 cm⁻¹, which correspond to the $\nu(^{13}\text{CO})$ isotopic analogs of the bands shown in Fig. 8b. Only the weak shoulder at 2055 cm⁻¹ in the product of the decomposition of normal isotopic CH₃OH does not appear in the ¹³CH₃OH analog. The $\nu(^{13}\text{CO})$ band corresponding to this 2055-cm⁻¹ feature would appear around 2010 cm⁻¹, but it was not detected, presumably because of its small relative intensity.

These results show that the four bands in the 2000-cm⁻¹ region are caused by ruthenium carbonyl species rather than ruthenium hydride, and that considering the previous $\nu(\text{CO})$ band assignments, some reduction occurs, directly or via CO and H₂O, during the methanol decomposition process in the PSSA–Ru film. The assignment of these bands to carbonyls was confirmed further by reaction of PSSA–Ru(III) films prepared using 25% deuterated methanol, CD₃OD, in D₂O solution. The resulting infrared spectrum was quite similar to that shown in Fig. 8b. Moreover, no evidence of Ru–D species was found in the region 1500–1350 cm⁻¹. There was a very weak band at 2261 cm⁻¹ due to $\nu(\text{C–D})$, since H–D exchange on the benzene rings occurs. Thus, it is clear that methanol is decomposed in the PSSA–Ru(III) films and results in Ru carbonyl species, but there was no evidence of the formation of Ru hydride or Ru formyl groups in the infrared spectra.

For the ethanol decomposition reaction, the ethanol-containing PSSA–Ru(III) films, prepared as described under Experimental, were heated to 117°C at 1×10^{-2} Torr for 6 days. Four bands at 2083, 2059 (sh), 2017, and 1970 cm⁻¹ were observed in the resulting infrared spectrum. This result is nearly identical to that of methanol decomposition reaction, although the relative intensities of the bands are different. When such films subsequently were exposed to ¹³CO, the ¹²CO species that had been formed upon the ethanol decomposition, exchanged with ¹³CO and yielded three bands at 2032, 1970,

and 1930 cm⁻¹, in excellent agreement with those found in the decomposition of ¹³CH₃OH.

Trial of Simple Static Fischer–Tropsch Reaction

Finally, simple static Fischer–Tropsch (F–T) type reactions were carried out by reacting PSSA–Ru(III) powder with CO (300 Torr) and H₂ (300 Torr) at 150°C for 3 days to test the potential for catalytic activity of PSSA-supported ruthenium in a preliminary way. The mass spectrum of the gas-phase products, obtained by trapping them in a liquid-nitrogen bath in order to remove the noncondensable unreacted CO and H₂ remaining after the reaction, indicates that a typical mixture of F–T reaction products of various aliphatic (C₁–C₄) hydrocarbon species and oxygen-containing compounds (aldehyde, ketone, and alcohol) was obtained.³

The infrared spectrum of the gaseous products agreed well with the mass spectral data. In the region of 3000 cm⁻¹, two medium absorption bands were observed at 2957 and 2875 cm⁻¹ due to asymmetric and symmetric stretching modes of CH₃ groups (Fig. 9) and at 2919 and 2851 cm⁻¹ due to in-phase and out-of-phase vibrations of CH₂ groups (30). Corresponding C–H deformation bands are observed at 1474, 1465, 1384, and 1375 cm⁻¹ and characteristic skeletal vibration bands at 1254 and 1167 cm⁻¹. Interestingly, there were two medium bands at 731 and 721 cm⁻¹ which arise from rocking modes of CH₂ groups of the type $-(\text{CH}_2)_n-$ ($n = 4$ or more), and this result suggests the formation of four adjacent straight chain hydrocarbon compounds which is in accord with mass spectral data. Functional group vibrations were observed at 3630 cm⁻¹ (OH stretching), 1750 cm⁻¹ (C=O vibration), 1067 and 1020 cm⁻¹ (C–O stretching modes). Further investigation of the catalytic use of PSSA–Ru

³ *m/e*; 12, 14, 15, 16, 22, 26, 27, 28, 29, 30, 31, 39, 41, 42, 43, 44, 45, 46, 48, 51, 53, 56, 57, 60, 64, 73, 78. Parent ion peak groups were detected at *m/e* 83, 85, 86.

ionomers is underway to determine actual product yields under controlled static and dynamic conditions.

CONCLUSIONS

Ru(III) ions have been incorporated in the ionic domains of sulfonated linear polystyrene to form PSSA–Ru(III) films with about 75% of the sulfonic acid groups of PSSA neutralized by Ru(III) ions. The reactions of PSSA–Ru(III) films with CO (400 Torr) in the temperature range 25–186°C resulted in four different Ru carbonyl species, which were characterized by typical infrared bands at 2150, 2085–2020, 2067–1985, and 2050–2001–1968 cm^{-1} , respectively. These Ru carbonyls are assigned to physically adsorbed CO in the PSSA–Ru, PSSA–Ru(II)(CO)₂, PSSA–Ru(II)(CO)₂, and PSSA–Ru(0)(CO)_n ($n = 1-4$), respectively.

Treatment of PSSA–Ru(III) film with hydrogen (400 Torr) at 150°C produced ruthenium hydride species and the corresponding ruthenium deuterides were identified in the infrared spectra. In addition, H–D exchange on benzene rings of the polystyrene backbone was found to occur during the reaction of PSSA–Ru(III) with D₂.

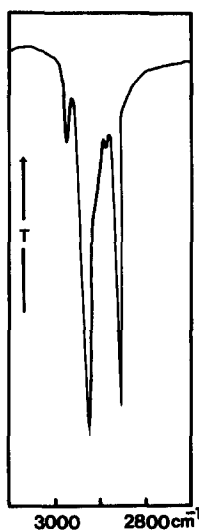


FIG. 9. IR spectrum of gaseous products from the static Fischer–Tropsch reaction.

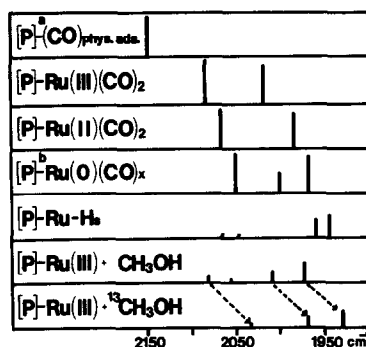


FIG. 10. Summary of IR spectral data and assignments for the PSSA(Ru) system: (a) physically adsorbed CO in PSSA–Ru(III) film, P = PSSA; (b) $x = 1-4$.

The reactions of aqueous methanol and ethanol on PSSA-supported Ru(III) produced ruthenium carbonyl species, but there was no evidence of ruthenium hydride or ruthenium formyl formations in the infrared spectrum. The assignments of all of the key spectral features discussed are summarized in Fig. 10.

Static Fischer–Tropsch type reaction on PSSA–Ru(III) powder with CO (300 Torr) and H₂ (300 Torr) at 150°C showed the formation of various aliphatic hydrocarbons, oxygen-containing hydrocarbon compounds, and CO₂. On the basis of these results, the PSSA-supported ruthenium may have useful catalytic activity in Fischer–Tropsch and methanol decomposition reactions under relatively mild conditions. Further studies involving PSSA-supported transition metals are in progress.

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