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Preparation of Ruthenium-Containing Polycarbonate Films and the Chemistry of Ruthenium in Polycarbonate

Il-Wun Shim,* Won-Suk Oh, Han-Cheol Jeong, and Won-Kyung Seok[†]

Department of Chemistry, Chung-Ang University, Seoul 156-756, Korea

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ABSTRACT: $RuCl_3 \cdot 3H_2O$ complexes have been incorporated into polycarbonate using solvent. The interactions between Ru complexes and polycarbonate (PC) are examined by infrared spectroscopy and thermal analysis. The reaction chemistries of these Ru-containing films have been investigated by reacting the Ru sites with CO, O_2, H_2, D_2, NO, and C_2H_4. They show interesting catalytic activities in various gas phase reactions under relatively mild conditions such as NO reduction, hydrogenation of ethylene and benzene, water-gas shift reaction, and oxidation of *n*-butyl sulfide.

Introduction

The studies of transition metal-containing polymeric materials have been a research area of current importance because of their versatile applications[1−3] as new materials. In these materials, it was well-known that incorporated transition metals gave rise to many useful physical and chemical properties of the polymers.[1,4,5] Our recent studies revealed that the metals themselves showed interesting catalytic reactivities under relatively mild conditions.[6−10] The most important feature of our research was that the chemical alteration of permeation selectivity of organic polymers could be realized by incorporation of reactive transition metal complexes into them; thus, it was possible to recover essentially pure H_2 gas from a 1:1 mixture of H_2 and CO gases using ruthenium-containing cellulose acetate membranes under ambient conditions.[11] This means that the transition metal-containing polymer films could be used for various gas separations.

In addition, those materials were thought to be a model for the development of the "reactive membrane"[12] which can function as both catalyst and separation medium, leading to a new catalytic system.[13,14] However, there have been only a few reports about the fundamental reaction chemistries of those transition metal-containing polymeric materials as well as comparative studies about their differences in different polymer matrices, which are believed to be very implemental to such developments.

In an attempt to extend our knowledge on this topic, $RuCl_3$ hydrate complexes have been incorporated into polycarbonate (PC), which is well characterized and known to have good membrane properties. Resulting Ru-containing PC films have been investigated to understand the interactions between Ru complexes and PC polymer molecules, the effect of the metal complexes, the thermal property of PC, and the reaction chemistry of the Ru complex in the PC polymer matrix. Results are reported in this paper.

Experimental Section

Pure polycarbonate (PC) and ruthenium-containing polycarbonate films (metal complex concentration: 10−40 wt %) were prepared as previously reported, using polycarbonate, $RuCl_3 \cdot 3H_2O$ (Aldrich), and tetrahydrofuran (Hayashi Pure Chemical Inc.) as a solvent.[9] For a typical preparation of 10 wt % Ru-containing PC films, 3.6 g of polycarbonate and 0.4 g of $RuCl_3 \cdot 3H_2O$ were dissolved in 100 mL of tetrahydrofuran, and the resulting mixture was boiled gently in the open for 15 min. After filtration of the solution, the filtrate was warmed at ca. 50 °C and the solvent was evaporated until the concentration of the solution reached ca. 12 wt %. After cooling to room temperature, the solution was cast on a glass plate using a scalpel. The thickness of the membranes was controlled in the range 20−90 μm, which is convenient for study by transmission infrared spectroscopy. After 5 h in air at room temperature, the brown homogeneous Ru-containing PC films (designated as [PC−Ru] films) were annealed at 110 °C for 1 day. These films are thermally stable up to 180 °C without deformation or decomposition, but at high metal concentration over 40 wt %, they become brittle and useless.

In this study, infrared spectroscopic analysis was quite helpful, especially in following the reaction chemistry of Ru in PC and analyzing gas phase reaction products. Also, various known infrared spectra[15] in the gas phase were very useful. Infrared spectra in the 4000−600 or 4000−250 cm^{-1} region were recorded on Hitachi I-3001, JASCO FT/IR 5300, and Nicolet MX-5 spectrometers. UV/vis spectra for elution tests were recorded on a Shimadzu UV-240 spectrometer. A series of measurements for the glass transition temperature (T_g) was carried out by using a DuPont Model 910 and General V4.1C thermal analyzer. In a typical differential scanning calorimeter (DSC) scan sequence, dq/dT was measured on heating 20 °C/min from 30 to 250 °C with 2 mV/cm sensitivity. The transmission electron microscopy (TEM) analyses were performed on a JEM-200CX microscope at 100 kV by direct observation to investigate the [PC−Ru] films after the reduction reactions with H_2 gas. The samples were prepared by embedding the films in epoxy resin and microforming them. The gases used in this work, carbon monoxide, hydrogen, deuterium, nitric oxide, oxygen, and ethylene of high purity grade, were purchased from Matheson. Most of the gas products were analyzed by gas chromatography (Shimadzu GC-R14). We used helium gas as a carrier gas and a 6 ft. copper column, containing a 5 Å molecular sieve with a TCD detector.

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* Author to whom correspondence is addressed.

[†] Department of Chemistry, Dong-Kuk University, Seoul 100-715, Korea

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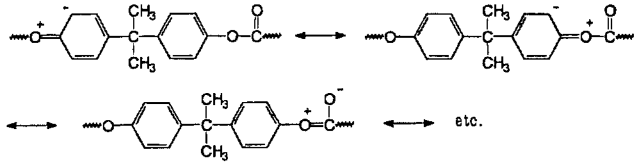
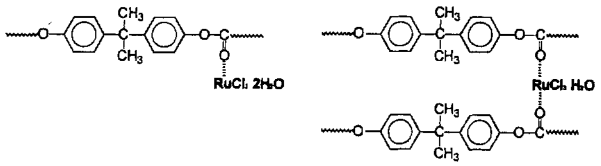
Results and Discussion

Interaction between Ru Complexes and PC. It was reported that when the solutions composed of cellulose acetate (CA) and $Cu(NO_3)_2$[16] or $RuCl_3{\cdot}3H_2O$[8] were cast into films, the electropositive Cu(II) or Ru(III) ions were assumed to coordinate to the oxygen atom of the acyl carbonyl group of CA. Such coordinations were evidenced from infrared spectroscopic studies. Quite similar interactions are presumed to occur between the Ru(III) ions and PC molecules on the basis of the hard character of the Ru(III) cation and the following electronic resonance of PC:



Thus, the electropositive Ru(III) will naturally interact with relatively electron rich oxygen atom(s) of the ester group of PC; in this case, the ν(C=O) stretching band of PC is expected to shift to a lower frequency and the other ν(C—O) stretching band to a higher frequency. In a typical infrared spectra of 10 wt % [PC—Ru] films, there are no bands due to the Ru complex in the 4000–600 cm^{-1} region. But the ν(C=O) band of PC at 1771 cm^{-1} shows a red shift of about 41 cm^{-1} and the band at 1200 cm^{-1} due to the ν(C—O) of PC broadens to a higher frequency of about 1250 cm^{-1}. These changes in infrared spectra, which are quite analogous to those of the aforementioned Ru(III), or Cu(II) in CA cases, are noticeable as the metal concentration increases from 5 to 30 wt %, but become weak at higher metal concentrations over 40 wt % since the intensities of the infrared bands arising from PC decrease, owing to the relatively decreased concentration of PC itself in the films. Accordingly, the incorporated Ru metal complexes are believed to interact with PC molecules as below:



In the far-infrared region, one weak band is observed at 327 cm^{-1} which can be easily assigned to linear ν(Ru—Cl),[17] suggesting that there is no formation of Cl-bridged dimer or oligomer ruthenium complex species in PC during the incorporation process.

***T_g* of Ru-Containing PC films.** As noted above, the oxygen atoms of ester groups of PC are believed to coordinate, at least partially, to Ru metal cations, and consequently, the PC molecules are expected to be cross-linked to a certain degree through such coordinations, leading to an increase in the glass transition temperature (T_g).[6-10,18] As expected, the T_g of [PC—Ru] films increases as below:

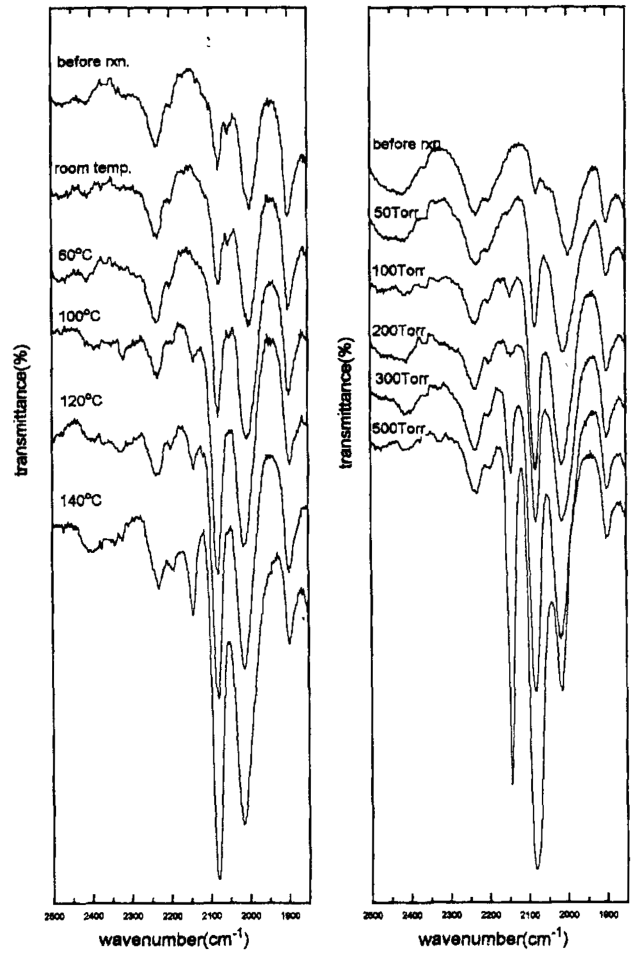
films	T_g, °C
pure PC	150
10 wt % [PC—Ru]	233
20 wt % [PC—Ru]	231
30 wt % [PC—Ru]	231
40 wt % [PC—Ru]	227

This result reveals that there are quite strong interactions between Ru metals and PC molecules, and this is not surprising, considering the high coordinating ability of ruthenium and high polarizability of PC molecules. In the case of 40 wt % [PC—Ru] films, the T_g decreases and the metal complexes at this high metal concentration are assumed not to act as cross-linking agents any more, but rather exist as impurities, resulting in a decrease of T_g. Therefore, we used 10 or 20 wt % [PC—Ru] films in this study.

Behavior of [PC—Ru] Films in Various Solutions. When 10 wt % [PC—Ru] films are immersed in water, aqueous 0.01 M NaOH, or 0.1 N KCN solution at room temperature for 24 h and dried at 110 °C in vacuum for 24 h, the films remain unchanged in appearance and infrared spectra, but UV/vis spectroscopic analyses for the aqueous solution indicate that about 10 wt % of Ru metals in PC are extracted from the PC matrix. The elution of Ru metals in solution is rather small, compared to the large solubility of the $RuCl_3{\cdot}3H_2O$ complex in water, but seems to be reasonable considering the strong interactions, as discussed above. Also, there was no substitution reaction of chloride by hydroxide or cyanide ions in solutions. It is worth pointing out that chloride ligand substitution by the cyanide ion occurred in the same Ru metal-containing cellulose acetate films under the same conditions, indicating that there is a significant difference in the chemistry of a transition metal complex depending upon polymer matrices. In aqueous 10 wt % NH_4OH or NaOH solution, the films are completely decomposed, and after dipping in methanol and ethanol, the films become quite brittle; accordingly, the [PC—Ru] films cannot be used in those solutions.

Reactions of Ru in PC with CO, O_2, and H_2 Gas Molecules. Heterogeneous reactions of Ru metals on inorganic oxide supports, such as Al_2O_3, SiO_2, TiO_2, and MgO, have been extensively studied in the last decades, and there are numerous reports about CO adsorption on oxide-supported Ru. In their infrared spectra, several CO adsorption bands appear consistently in three regions: 2020–2050, 2060–2090, and 2125–2160 cm^{-1}; the low-frequency bands are typically assigned to carbonyls adsorbed on reduced Ru, the medium bands to those on oxidized Ru, and the high-frequency bands to CO molecules adsorbed on ruthenium oxide or physically adsorbed CO on the surface.[19-21] However, there are a few reports about CO adsorptions on polymer-supported Ru. Recently, we reported a series of Ru(III), Ru(II), and Ru(0) carbonyls formed in sulfonated linear polystyrene,[22] cellulose acetate (CA),[8] and polysulfone (PS)[10] on the basis of various systemic experimental results, including stepwise reductions and corresponding oxidation reactions in reverse order. These facts are a useful starting point to consider the reaction chemistry of Ru in PC with CO gas.

When the 10 wt % [PC—Ru] films, dried at 110 °C in vacuum for 1 day are treated with CO (700 Torr) at 140 °C for 1 day, three strong ν(CO) bands are observed at 2144, 2080, and 2016 cm^{-1} (see Figure 1), which are similar to those of Ru—carbonyls formed in CA[8] and PS.[10] The band at 2144 cm^{-1} is assigned to physically adsorbed CO on Ru(III) metals since it appears at a higher reaction temperature than the other two bands and disappears quite rapidly under vacuum or upon reaction with O_2, N_2, or H_2 gases. When the films are treated with CO gas even at room temperature for



(a) (b)

Figure 1. IR spectra of CO adsorption on Ru sites in PC: (a) as a function of reaction temperature (CO: 700 Torr); (b) as a function of reaction of CO gas pressure (at 140 °C).

several days, there are only two bands at 2080 and 2016 cm^{-1}. The two bands at 2080 and 2016 cm^{-1}, which appear simultaneously upon reaction with CO gas, are quite stable in air or vacuum and are inert to reaction with O_2 or N_2 (600 Torr) at 140 °C. Also their shapes and band intensity are analogous to those of well-characterized *cis*-Ru^{III}(CO)$_2$ species.[8,10,22] From the intensity ratio of the two bands (ν_s 2080, ν_{asym} 2016), the CO–Ru–CO angle is calculated to be around 81°. When those [PC–Ru] films are consecutively exposed to O_2 (700 Torr) gas at 160 °C, for 1 day, the intensity of the 2144 cm^{-1} band decreases significantly but the other two bands remain unchanged. The gas product for this reaction is easily identified to be CO_2.[15] Accordingly, the physically adsorbed CO species on Ru(III) sites are believed to be the only active carbonyl under the described conditions. In order to test the possibility of further oxidation of Ru(III), the same film is re-treated with CO (700 Torr) at 160 °C; the same three bands are observed at the same positions, and this result denotes that there is no further oxidation under these conditions. Thus, the bands at 2080 and 2016 cm^{-1} are assigned to *cis*-PC–Ru^{III}(CO)$_2$ and the band at 2144 cm^{-1} is assigned to physically adsorbed CO on a Ru(III) site.

In order to examine the reduction possibility of Ru(III) in PC, new [PC–Ru] films are reacted with H_2 gas (700 Torr) at 160 °C for 1 day; there is an infrared band at 1974 cm^{-1} which can be attributed to the ruthenium hydride stretching mode. It is noteworthy that there are no reports of the direct observation of ruthenium hydride species on inorganic oxide supports even though they are assumed to exist as an important intermediate in various catalytic reactions. Recently, we reported rhodium[6] and palladium[7] hydrides in various polymers and they were found to have catalytic activities for hydrogenation of olefin or nitric oxide reduction reactions.[13] When the films, after reaction with H_2 gas, are consecutively treated with CO (700 Torr) at 160 °C, there are four new ν(CO) bands at 2133, 2074, 2040, and 2006 cm^{-1} in addition to the three bands at 2144, 2080, and 2016 cm^{-1} (see Figure 2). The intensity of the band at 2133 cm^{-1} is quite sensitive to reaction with O_2 or H_2 or even in vacuum, just like the band at 2144 cm^{-1}. Accordingly, this is assigned to physically adsorbed CO on reduced Ru metals. The positions and intensities of the 2074, 2040, and 2006 cm^{-1} bands varied depending upon the reduction reaction time and temperature with H_2 gas, indicating that these are originating from reduced Ru carbonyls. But, the band at 2040 cm^{-1} appears in the infrared spectra after a relatively longer reduction reaction with H_2 gas in comparison to the other two bands and completely disappears upon reaction with O_2 gas, suggesting that this is arising from Ru(0) monocarbonyl in PC. The ν(CO) bands due to Ru(0) monocarbonyl typically appeared in the 2040–2050 cm^{-1} region.[19-21] In the case of two bands at 2074 and 2006 cm^{-1}, they appear

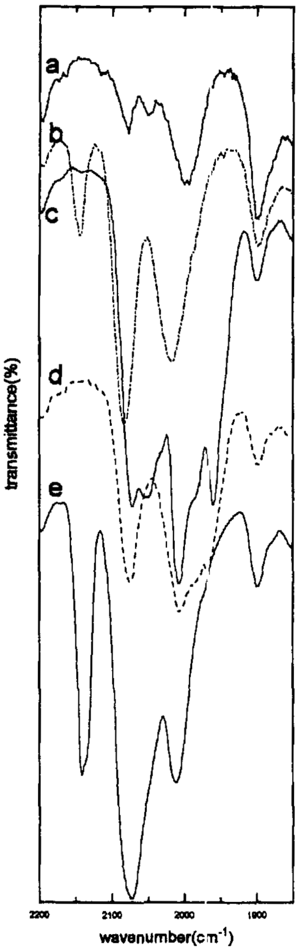


Figure 2. IR spectra for the reduction reaction (gas pressure, 700 Torr; 180 °C, 1 day): (a) 10 wt % [PC–Ru] film; (b) after reaction with CO; (c) after reaction with H_2; (d) (c) after reaction with O_2; (e) (d) after reaction with CO.

Table 1. Summary of Ru Carbonyl, Nitrosyl, and Hydride Species Formed in Polycarbonate

ν(CO) or ν(Ru−H) or ν(NO) in cm^{-1}	assignment
2144	physically adsorbed CO on Ru(III) sites
2133	physically adsorbed CO on Ru(II) sites
2080, 2016	*cis*-PC−Ru^{III}(CO)$_2$
2070, 2006	*cis*-PC−Ru^{II}(CO)$_2$
2040	PC−Ru(0)(CO)
1974	PC−Ru hydride
1985, 1960	PC−Ru dihydride
1897	PC−Ru^{III}(NO)
1882	PC−Ru^{II}(NO)

simultaneously and their intensities increase on further reaction with H_2. But they are inert to O_2 gas. Thus, these two bands at 2070 and 2006 cm^{-1} are reasonably assigned to *cis*-PC−Ru^{II}(CO)$_2$.

In order to confirm this assumption, another [PC−Ru] film was reacted with CO (700 Torr) at 160 °C for 1 day and then, after evacuation of the CO gas, reexposed to H_2 gas under the same conditions. In the infrared spectra, there are two strong ν(CO) bands at 2070 and 2006 cm^{-1} in addition to other bands at 2144, 2133 (sh), 2080 (sh), 2040 (sh), 2016 (sh), and 1974 (sh) cm^{-1}, as already discussed. Upon further reduction at a higher temperature (180 °C), the band at 2040 cm^{-1}, arising from Ru(0)−(CO) species, becomes noticeable, and there are two new strong bands at 1984 and 1960 cm^{-1}. These two bands are believed to originate from Ru dihydride. The Ru dihydride was reported to be easily formed when some carbonyl ligands are coordinated to the same Ru metals since the carbonyl ligands stabilize ruthenium hydride bonds.[23] To find corresponding Ru deuterides, [PS−Ru] films are treated with D_2 gas; there are three bands at 1400, 1390, and 1366 cm^{-1} in the difference infrared spectrum taken before and after the reduction reaction, but their intensities are too weak and unreliable. After such reduction reactions, the films are examined by transmission electron microscopy (TEM), but no ruthenium metal particles or metal clusters are observed within the resolution limit of 10 Å, and in far-infrared spectra, the intensity of the ν(Ru−Cl) band at 327 cm^{-1} decreases about 70%, indicating that there is appreciable reduction of Ru cations. The frequencies of the Ru carbonyls and hydrides discussed here are listed in Table 1.

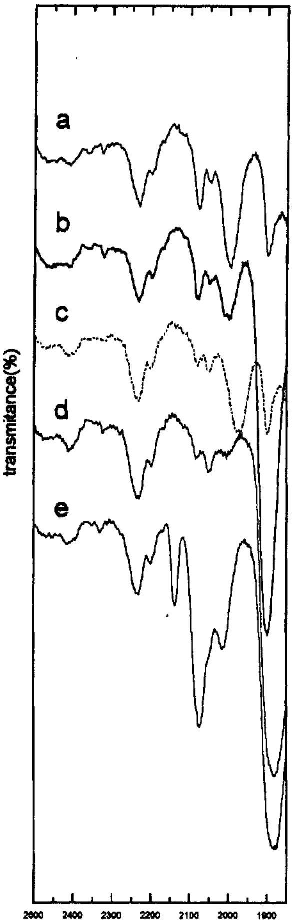


Figure 3. IR spectra of Ru nitrosyl, hydride, and carbonyls: (a) 10 wt % [PC−Ru] film: (b) after reaction with NO (700 Torr) at room temperature; (c) after reaction with H_2 (700 Torr) at 160 °C; (d) (c) after reaction with NO (300 Torr) at 160 °C; (e) (d) after reaction with CO (300 Torr) at 160 °C.

Reaction of Ru in PC with O_2 and NO Gases. As described in the previous section, there is no oxidation of Ru(III) in PC by reaction with O_2 under the described conditions, and physically adsorbed carbonyls and Ru(0) monocarbonyls at 2040 cm^{-1} are found to be reactive with O_2 gas, resulting in the production of CO_2. The oxidation possibility of Ru(II) or Ru(0) species to Ru(III) or Ru(II) formed in PC is examined by reacting the films with O_2, CO, O_2, CO, and O_2 gases, consecutively. But there is no evidence for such an oxidation.[20] Coordination of molecular oxygen to Ru metals[17] in PC or formation of ruthenium oxo (Ru═O)[17,24] species after reaction with aqueous H_2O_2 was investigated by UV/vis and infrared spectroscopy, but failed. In addition, catalytic oxidation of CO with O_2 gas is tested by reacting a 2:1 mixture of 0.2 g of [PC−Ru] film CO and O_2 gas (total pressure: 600 Torr) at 180 °C for 5 days in a static state, but only a very small portion of CO was converted to CO_2. This result is in striking contrast to the case of the same Ru complex-containing cellulose acetate, in which CO gas molecules were completely oxidized to CO_2 under the same conditions. At this moment, the reason is not known.

When dehydrated [PC−Ru] films are exposed to NO gas (600 Torr) at room temperature for 1 day, a very strong ν(NO) band is observed at 1897 cm^{-1} (see Figure 3), which is easily assigned to Ru(III) nitrosyl species with linear geometry.[17,25] It is very stable in air or vacuum at 140 °C. When the films are consecutively reacted with H_2, there is no ν(Ru−H) band and only the ν(NO) band decreases by about 20%, indicating that almost all of Ru(III) cations in PC react with NO molecules and that there is no reductive nitrosylation reaction.[26]

When a [PC−Ru] film, pretreated with H_2 (700 Torr) at 160 °C for 1 day, is exposed to NO gas as above, a strong ν(NO) band appears at 1882 cm^{-1} but there is no ν(Ru−H) band at 1974 cm^{-1} in the same IR spectrum (See Figure 3). This result reveals that the ν(NO) band originates from NO molecules coordinated on reduced Ru in PC and that there is no formation of HRu(NO) type species in PC. When the film is consecutively reacted with CO gas (700 Torr) at 160 °C for 1 day, there are three distinct ν(CO) bands at 2133, 2070, and 2006 cm^{-1} as well as other weak ν(CO) bands, as described in an earlier section. Also, the intensity of the ν(NO) band at 1882 cm^{-1} decreases about 8%, but the position remained unchanged; this means that the 1882 cm^{-1}

band comes from Ru(II)−NO species in PC and that no (CO)Ru(NO) type species is formed in PC under the conditions.

Water-Gas Shift Reaction with [PC−Ru] Films. It is well-known that the ruthenium metal complexes possess catalytic reactivity in water-gas shift reactions.[20,27] In order to test this possibility in a preliminary way, a mixture of CO (600 Torr) and a slight excess of H_2O (8 mL) is reacted in a flask at 140 °C and the whole system is insulated to avoid condensation of water. The reaction mixture is frequently monitored by gas phase IR spectroscopy.[15] During the reaction, the intensity of the band due to CO gas at 2143 cm^{-1} gradually decreases and those of the bands due to CO_2 gas correspondingly increase. After a 13 day reaction, the conversion is completed and the turnover number, based on the assumption that all Ru metals in PC are reactive, is about 0.58 (unit: substrate molecules transformed per metal atom per hour). The IR spectrum of the [PC−Ru] film after the reaction shows no other species than the aforementioned Ru carbonyls and hydride, suggesting that some dissociation of water molecules is involved in the reaction.

Reduction of NO by H_2 or CO Gas with [PC−Ru] Films. For the reduction reaction, a mixture of NO (50 Torr) and H_2 (150 Torr) gases is introduced into a 500 mL flask with 0.1 g of [PC−Ru] films and heated at 180 °C. After a 2 day reaction, complete conversion of NO to N_2O is observed:

$$2NO + H_2 \rightarrow N_2O + H_2O$$

In this experiment, the reactant and product are easily identified by their characteristic IR bands:[15,17] NO, 1880 cm^{-1}; N_2O, 2230 cm^{-1} (H_2O, trapped by Drierite gas-drying units). The turnover number calculated as in the water-gas shift reaction is about 0.31. In IR spectra of the films after reaction, surprisingly there is only a band at 1882 cm^{-1} due to Ru(II)−(NO) species. There is no evidence for the well-known NO dissociation,[13,28,29] nor for the formations of $Ru(NO)_2$[30] and RuH(NO) species in the PC films. This means that in the [PC−Ru] films, NO reduction by H_2 proceeds by a different mechanistic pathway compared with those of known inorganic oxide-transition supported metal catalysts.[28,29] It is believed that direct attack of hydrogen gas molecules to a coordinated nitrosyl group on Ru sites is involved in this reaction. In addition, it should be noted that in the same Ru-containing cellulose acetate,[13] there was no NO reduction at all: in the case of polysulfone,[10] the product was found to be ammonia and H_2O under similar reaction conditions.

In an attempt to reduce NO with CO gas, a 1:2 mixture of CO and NO gases (total pressure: 90 Torr) is reacted at 180 °C. The products, after a 4 day reaction, are easily identified to be N_2O and CO_2, but only a small portion of NO is found to be converted even after a much longer reaction time. The [PC−Ru] films after this reaction are examined, but there are no new intermediates such as Ru−(CO)(NO)[30] species.

Hydrogenation of Ethylene and Benzene with [PC−Ru] Films. When a mixture of ethylene (200 Torr) and hydrogen (400 Torr) is treated with [PC−Ru] films at 180 °C, complete hydrogenation of ethylene to ethane is identified by comparing with known infrared spectra of ethylene and ethane after a 2 day reaction. The turnover number is estimated to be 1.26 on the same assumption as noted previously. The infrared spectrum of the [PC−Ru] films used in this reaction shows a weak band at 1974 cm^{-1} due to Ru hydride, but there is no evidence for ethylene molecules coordinated to Ru in PC.

Similarly, hydrogenation of benzene is tried by reacting benzene (3.6 mL) and H_2 gas (100 psi) in a Parr high pressure reactor at 150 °C. After a 2 day reaction, almost all of the benzene is converted to cyclohexane which is easily analyzed and identified by infrared[15] and NMR spectroscopy.[31] Partial hydrogenation of benzene to cyclohexadiene or cyclohexene is tried by using a stoichiometric amount of reactants, but after reaction, only cyclohexane is found in the product. This is quite analogous to the typical heterogeneous catalytic reaction without selectivity. In the infrared spectrum of the film after reaction, there is no evidence for benzene molecules coordinated to Ru metal in π donor type (η^2 or η^4 binding form)[32] except ruthenium hydride, as previously noted. In a separate experiment, reduced [PC−Ru] films by H_2 gas are reacted with benzene in the gas phase at 100 °C, and there is an oxidative addition reaction of benzene to Ru metal in PC with C−H bond breaking, which is identified in the infrared spectrum of the films (for coordinated benzene, 3090, 3071, 3036, 1479, 1035, 680, and 467 cm^{-1}; for Ru hydride, 1963 cm^{-1}). We tried the CO insertion reaction to ruthenium and phenyl bond by reacting the film with benzene (5 mL) and CO (140 psi) at 110 °C, but there was no such CO insertion product like benzaldehyde.[20] In this case, the product, formed on the surface of the reactor, was found to be $Ru_3(CO)_{12}$ in the crystalline solid state.[20]

Oxidation of *n*-Butyl Sulfide by O_2 with [PC−Ru] Films. The selective oxidation of sulfide to sulfoxides[33] is well-known to be important in modeling desulfurization reactions and for the synthesis of versatile sulfoxides. Recently, Friend and Bol proposed that oxidation of 2-propanethiolate on oxygen-covered Rh(III) proceeds through carbon−sulfur bond breakage, affording 2-propyl species, followed by rapid β-hyrogenation elimination to propene or oxygen addition to 2-propoxide.[34] A similar result was reported by Drago and Katritzky:[35] Ru complexes in polystyrene/silicone gum rubber composite membrane were found to oxidize *n*-butyl sulfide at 90 °C with O_2 (30 psi). The products were butyl sulfoxide, butyraldehyde, propionaldehyde, and a small portion of 1-butene and 1,2-epoxybutene, indicating that the C−S bond breaking is also occurring in this reaction. In this background, *n*-butyl sulfide (0.5 mL) was treated with O_2 (500 Torr) with the [PC−Ru] films at 90 °C for 2 days, and the resulting gas phase products are found to be butyraldehyde, CO_2, COS. (H_2O is trapped during the sampling process.) In the gas phase infrared spectra, there is no evidence for sulfoxide, nor olefin formation, and this result, although quantitative analysis and mechanistic study in detail are not carried out, is interesting in that at least one C−S bond is not broken during the reaction compared with the above cases.

Conclusion

$RuCl_3 \cdot 3H_2O$ complexes have been incorporated into PC without introduction of typical pendant ligand groups to the polymer backbone, and the resulting brown transparent films with 10−30 wt % Ru complex loading are quite thermally stable up to 180 °C. On the basis of infrared spectral and thermal analysis data, the ruthenium metal complexes are supposed to coordinate, at least partially, to the acyl oxygen atom of ester groups in PC and to act as cross-linking agents between PC molecules. The reaction of 10 wt % [PC-Ru] films with CO and/or H_2 gas at 160 °C results in various Ru carbonyl species in PC, which are assigned to *cis*-PC$-$Ru^{III}(CO)$_2$ (ν(CO): 2080, 2016 cm^{-1}), *cis*-PC$-$Ru^{II}(CO)$_2$ (ν(CO): 2070, 2006 cm^{-1}), PC$-$Ru^0(CO) (ν(CO): 2040 cm^{-1}), and physically adsorbed CO on the Ru(III) or Ru(II) metal sites (ν(CO): 2144 and 2133 cm^{-1}, respectively). The Ru(III) or Ru(II) dicarbonyl species are inactive in the reaction with O_2 or H_2 gases. Treatment of the [PC$-$Ru] films with H_2 gas gives rise to partial reduction of Ru(III) cations to Ru(II) or Ru(0) and produces stable ruthenium monohydrides (ν(Ru$-$H): 1974 cm^{-1}) and dihydrides (ν(Ru$-$H): 1985, 1960 cm^{-1}). But there is no evidence for the formation of metal cluster or particles bigger than 10 Å in diameter. Two ruthenium nitrosyl species are characterized and assigned to PC$-$Ru^{III}NO (ν(NO): 1897 cm^{-1}) and PC$-$Ru^{II}NO (ν(NO): 1882 cm^{-1}).

The ruthenium metal complexes incorporated into PC are found to have interesting catalytic reactivities under relatively mild conditions in NO reduction, hydrogenation of ethylene and benzene, water-gas shift reaction, and oxidation of *n*-butyl sulfide. It is noteworthy that the reaction chemistries of the same Ru complexes vary, depending upon the polymer matrix, indicating that there are significant effects of the polymer matrix on them. In addition, surprisingly, no typical surface intermediates arising from NO dissociation are observed in PC films during the NO reduction reaction, suggesting that direct attack of H_2 or CO gas molecules on coordinated nitrosyl groups in PC might be involved in the reaction. Further studies for the applications of using these [PC$-$Ru] films, including gas separation and development of so-called reactive membranes, are in progress.

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