

Preparation of Iron Nanoparticles in Cellulose Acetate Polymer and Their Reaction Chemistry in the Polymer

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Recently, intense research efforts have been focused on the design and fabrication of inorganic nanoparticles in polymers because of their novel electronic, optical, magnetic and chemical properties.¹⁻³ These methods, exploiting polymer matrix, have been reported to have relatively better control over nano metal cluster formation.⁴ Also, these nanoscale materials in polymers exhibit a variety of useful potential applications in catalysis, magnetism, and gas separation.⁵ We have reported on the preparations of Rh, Ru, and Pd nanoparticles formed in various polymers such as cellulose acetate, polycarbonate, and polysulfone in addition to their reaction chemistry.^{6,7} In the preparation of these inorganic-organic nano composite materials, an important task is the prevention of both phase separation and aggregation of the metal clusters in the polymer matrix. In addition, it is noteworthy of attention that the host polymer matrix itself significantly affects on both the formation of nano metal clusters and their reaction chemistry in the polymer. However, there have been only a few systemic comparative studies on these aspects. In an effort to extend our knowledge on these subjects, various iron metal complexes such as FeCl₃, γ -Fe₂O₃, Fe(CO)₅, and Fe₃(CO)₁₂ have been incorporated into cellulose acetate (CA) and the resulting Fe-containing polymeric films have been investigated to understand the interactions between the Fe complexes and CA, the formation of Fe nanoclusters with their size control, and their reaction chemistry in polymer host.

Experimental Section

Pure cellulose acetate (CA) and iron-containing cellulose acetate films (metal complex concentration: 5-20 wt.%) were prepared as previously reported,⁵⁻⁷ using cellulose acetate, FeCl₃·6H₂O, γ -Fe₂O₃, Fe(CO)₅, Fe₃(CO)₁₂ (Aldrich) and tetrahydrofuran or methoxyethanol (Hayashi Pure Chemical Ind.) as a cosolvent. For a typical preparation of 10 wt% Fe-containing CA films (designated as 10 wt% [CA-Fe] film), 3.6 g of cellulose acetate and 0.4 g of Fe-complex compound were dissolved in 100 mL tetrahydrofuran, and the resulting mixture was boiled gently in the fume hood for 15 min. Then, the solvent was evaporated until the concentration of the solution reached *ca.* 12 wt%. After cooling to room

temperature, the solution was cast on the glass plates using a scalpel. The thickness of the films was controlled to 50-90 μ m, which is convenient for transmission infrared spectroscopy. In this study, infrared spectroscopy is quite helpful in following gas phase reaction process and analyzing gas products on the basis of well known infrared spectral data. The [CA-Fe] films containing FeCl₃·6H₂O, or Fe(CO)₅, or Fe₃(CO)₁₂ are light brown colored and transparent. In case of γ -Fe₂O₃-containing CA films, which are superparamagnetic,⁸ their brown color become dark and opaque as metal concentration increases. They are thermally and mechanically stable up to 180 °C, but at high metal loading over 20 wt%, they become quite brittle after reaction with H₂ gas at 150 °C. Infrared spectra in 4000-250 cm⁻¹ region were recorded on Jasco FT/IR 5300, and Nicolet MX-5 spectrometer. UV/Vis spectra for elution tests were recorded on Shimadzu UV-240 spectrometer. Thermal properties of the films were examined by Setaram LABSYS analyzer and transmission electron microscopy (TEM) were performed on a JEM-200CX microscope to observe iron metal particles in CA. Most of the gas products were analyzed by Shimadzu GC-R14 and Donam GC. For high pressure gas phase reactions, Parr reactors were used with automatic temperature control systems.

Results and Discussion

The interactions between Fe(III) complexes and CA molecules can be considered as electrostatic in nature, namely, ion-dipole interactions. Accordingly, the electron-rich oxygen atoms of polar hydroxyl and/or acetate groups of CA are expected to interact with electropositive transition metal cations. This assumption was evidenced in the infrared spectroscopic studies of hard Be(II), Mg(II) metal cation-containing CA.⁹ In these cases, both the hydroxyl and the acyl carbonyl absorption bands (at 3500 and 1750 cm⁻¹, respectively) undergo the red shifts indicative of band weakening due to the competition of the metal cations for the electrons of which the bonds are composed. In a typical infrared spectra of FeCl₃·6H₂O-containing CA films, the characteristic bands due to coordinated water molecules are observed at 3500 and 1640 cm⁻¹ in addition to the bands from CA molecules, and their intensities increase as the Fe metal loading increases. But when these films are heated at 100 °C in vacuum for 1 day, as expected, both the two aforementioned hydroxyl and the acyl bands broaden to

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lower frequencies at 3300 and 1700 cm^{-1} , respectively, indicating that there are appreciable interactions between Fe(III) metal cations and the oxygen atoms of both hydroxyl and acyl groups in CA. Of course, such interactions could occur on an intermolecular way and the CA molecules are thought to be cross-linked through such interactions or at least partial coordinations, resulting in the increase of glass transition temperature (T_g) of CA polymer. As predicted, the glass transition temperatures of 10 wt% [CA-Fe] films increase by 20-25 $^{\circ}\text{C}$ compared to that of pure CA films. In case of light brown colored transparent $\text{Fe}(\text{CO})_5$ and $\text{Fe}_3(\text{CO})_{12}$ -containing CA films, corresponding $\nu(\text{CO})$ bands around 2100-1800 cm^{-1} region are observed right after they are cast. But upon gas phase reaction with O_2 at 100 psi, or heating under the vacuum at 100 $^{\circ}\text{C}$, they are gradually disappeared and a new $\nu(\text{CO})$ band appears at about 1560 cm^{-1} , which is believed to arise from the carbonyls multiple-bridged to iron metal atoms, or trapped in the metal clusters in CA. When 20 wt% [CA-Fe] films are treated with H_2 gas (150 psi) at 100-150 $^{\circ}\text{C}$, or heated in vacuum at 100 $^{\circ}\text{C}$ air for one day, the $\nu(\text{CO})$ band disappears. In a transmission electron micrograph of these films, iron metal clusters of about 80-110 \AA in diameter are observed with narrow size distribution as shown in Figure 1. The size of metal particles is found to be controlled to the range of 30-150 \AA by adjusting metal concentration in CA or thermal heating conditions. Surprisingly, these iron metal particles are found to be chemically quite stable; when the iron cluster-containing CA films are treated with O_2 gas or CO gas (150 psi, at 100-150 $^{\circ}\text{C}$), there are no changes in the films at all, nor any evidences for the formation of iron oxides (FeO , or $\gamma\text{-Fe}_2\text{O}_3$), or iron carbonyl species such as $\text{Fe}(\text{CO})_5$, $\text{Fe}_2(\text{CO})_8$, and $\text{Fe}_3(\text{CO})_{12}$. But after prolonged (more than 4 days) reaction with O_2 gas at the same conditions as above, or upon treatment in aqueous H_2O_2 solution, only a trace amount of FeO_2 is found to be produced in the film, which is evidenced by its characteristic IR band at 800 cm^{-1} due to peroxide species.¹⁰ This result is in a striking contrast to the case of $\text{Fe}(\text{CO})_5$ adsorbed in poly(tetrafluoroethylene) (PTFE) polymer;¹¹ The latter was



Figure 1. Transmission electron micrograph, showing Fe nanoparticles of 80-110 \AA in diameter in a cellulose acetate film

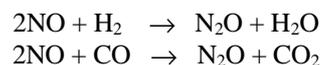
completely oxidized in air, forming an iron oxide-composite material, which is known to be superparamagnetic. For comparison, $\gamma\text{-Fe}_2\text{O}_3$ dissolved in tetrahydrofuran is incorporated into CA polymer as described in the experimental section; This kind of iron oxide-polymer composite has been received much attention since it can be used for optical recording media.⁸ When they are treated with H_2 gas (150 psi) at 125 $^{\circ}\text{C}$ for more than 4 days, there is no appreciable reduction reaction in the films at all, showing that the Fe_2O_3 in CA is quite inert at the described conditions. However, when 10 wt% FeCl_3 -containing CA films are treated in the same way as above, they become dark black and shiny, indicating that the iron cations are reduced to Fe metal particles of which size is about 30-50 \AA ; a consecutive reoxidation reaction of these films with O_2 gas at the similar condition as above was tried but failed. Thus, iron nanoparticles are found to be formed in CA upon reduction reaction or simple thermal heating, but they are not reoxidized under the described conditions. These small iron particles in CA are expected to perform a variety of catalytic reactions. To test this potential in a preliminary way, several catalytic reactions are carried out in a static state.

Water-gas shift reaction. A 1 : 1 mixture of CO and H_2O (total gas pressure 150 psi) is reacted in a Parr reactor at 120 $^{\circ}\text{C}$ with 0.1 g of [CA-Fe] film and about 60% of CO is found to be converted to CO_2 and H_2 gas on the basis of IR spectroscopy and GC analysis. There is no noticeable decrease of catalytic activity of the [CA-Fe] films after repeated reactions. But no iron-carbonyl; nor -hydride species is identified during the reactions in the CA films.

CO oxidation by O_2 gas. Complete conversion of CO to CO_2 is confirmed by reacting a 2 : 1 mixture of CO and O_2 gas at the same conditions as above. Even in low gas pressure reaction (total pressure : 600 torr), the same result is observed. However, no iron oxide formation in CA is observed as discussed in the earlier section.

Hydrogenation of ethylene, benzene, and styrene monomer. Upon hydrogenation reaction of ethylene, benzene, and styrene monomer at the same conditions as above (total pressure : 150 psi), their products are found to be ethane, cyclohexane, and ethyl benzene, respectively, and these products are easily confirmed by their characteristic IR spectra and NMR (Varian Gemini 2000 (300 MHz)). During the reaction, the gas phase reaction mixture was carefully monitored to find other possible products such as cyclohexene, cyclohexadiene, and ethyl cyclohexane but failed, denoting that this reaction system is a typical case of simple heterogeneous catalytic reaction.

Reduction of NO by H_2 or CO gas. It is well known that NO gas is catalytically reduced by CO or H_2 gas and the products are usually N_2O , NH_3 , and N_2 . After 7 day reaction of NO with H_2 or CO at the similar conditions as above (total gas pressure; 600 torr), about 80% NO is converted to N_2O as below:



However, there is no product dependence upon the hydrogen gas pressure; at higher H₂ gas pressure, there is no N₂, nor NH₃ gas product formation. When the [CA-Fe] films after these reactions are examined, only a $\nu(\text{NO})$ band at 1580 cm⁻¹ which can be assigned to bridged nitrosyl species¹⁰ is observed, but there are no other evidences for the well known NO dissociation reactions,¹² suggesting that direct attacks of H₂ or CO molecules to the coordinated nitrosyl groups on Fe metal sites.^{6,7}

Conclusions

Various iron metal complexes have been incorporated into CA films as a dispersion medium. The resulting homogeneous films of 5-20 wt% Fe metal complex concentration are found thermally stable up to 150 °C and the relatively electron rich oxygen atoms of hydroxyl and acyl groups in CA molecules are assumed to interact with Fe complexes on the basis of their infrared spectroscopy and thermal analysis. These interactions are quite noticeable in Fe(III)-containing CA films. The treatment of [CA-Fe] films with H₂ gas at 120 °C, or heating in vacuum, produces small Fe metal particles about 80-110 Å in diameter in CA with relatively narrow size distribution, and their size is found to be controlled to the range of 30-150 Å by adjusting metal concentration in CA film or heating conditions. These small Fe metal particles show various catalytic reactivities such as water-gas shift reaction, CO oxidation, NO reduction, and hydrogenation of olefins under relatively mild conditions.

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