

Preparation of Silver Nanoparticles in Cellulose Acetate Polymer and the Reaction Chemistry of Silver Complexes in the Polymer

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Polymer/inorganic composites have been an active research subject of great practical importance in last decades because of their interesting physicochemical properties.¹ Also, these materials received attention in the search of practical methods for the synthesis of various inorganic nanoparticles, which were reported to have more controls over cluster formation, their size and shape, and their size distribution.²⁻⁴ We reported a series of articles about the preparation of Ru, Rh, Pd, Fe, and Cu metal nanoparticles in various polymers such as cellulose acetate, polycarbonate, polysulfone, and silicon rubber in addition to their reaction chemistry; the transition metal nanoparticles in those polymer matrices showed quite interesting chemical and/or catalytic reactivity toward various small gas molecules under relatively mild conditions, which are quite different from those of corresponding free transition metal complexes or from those in inorganic oxide-supported systems.⁵⁻⁸ In general, the inert polymer itself was found to significantly affect on the reaction chemistry of various transition metal complexes in the polymer although there are only a few systemic comparative studies on this subject. Meanwhile, it is well known that silver is superior to other metals in electrical property, antimicrobial effect, optical properties, and oxidation catalysis.⁹ Besides, silver-containing polymer membranes were reported to be used as light olefin/paraffin separation membranes through selective adsorption process.¹⁰

In this background, silver nitrate has been incorporated into cellulose acetate (CA) polymer as a dispersion medium and these silver-containing polymer films are investigated to understand the interactions between silver complexes and cellulose acetate molecules, the formation of Ag nanoparticles with their size control, and their reaction chemistry in cellulose acetate polymer.

Experimental Section

Pure cellulose acetate (CA) and silver-containing CA films (metal complex concentration: 5-20 wt.%) were prepared as previously reported,^{6,9} using cellulose acetate, AgNO₃ (Aldrich), and 2-methoxyethanol (Aldrich). For a typical preparation of 10 wt.% silver acetate-containing CA films (designated as 10 wt.% [CA-Ag] film), 3.6 g of cellulose acetate and 0.4 g of AgNO₃ were dissolved in 100 mL 2-methoxyethanol, 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 20-90 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.¹¹ These Ag-containing films are light brown colored and transparent. They are thermally and mechanically stable up to 200 °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 a Jasco V-550 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 silver metal particles in CA. Various gas products were analyzed by Donam G/C, Autospec EBE GC/Mass spectrometer, and gas phase FT-IR spectroscopy. For high-pressure gas phase reactions, Parr reactors were used with automatic temperature control systems.

Results and Discussion

In the typical infrared spectra of silver containing CA films, there are several characteristic bands due to nitrate at 1774, 1750, 1390, and 810 cm^{-1} as well as the bands from CA. These bands from silver nitrate increase in their intensities as the silver metal concentration increases, and there are no changes in their positions after incorporated into CA polymer indicating that their structure remains unchanged in CA; in this case, the nitrate anions are assumed to exist as bridging ligands.¹² Meanwhile, considering that the possible interactions between silver nitrate and CA molecules are expected to be basically electrostatic in nature, namely, ion-dipole interactions, the electron-rich, oxygen atoms of acetate groups in CA molecules are assumed to interact with electropositive silver metal cations. This assumption was verified by the careful infrared spectroscopic study of silver-containing CA films; the characteristic $\nu(\text{C}=\text{O})$ band of pure CA at 1748 cm^{-1} shows a slight red shift to 1744 cm^{-1} upon incorporation of silver cations into CA, indicating C=O bond weakening, and correspondingly,

ν (C-O) band of acetate group at 1235 cm^{-1} is shifted to a higher frequency at 1239 cm^{-1} . These interactions are quite weak in comparison to other transition metal complex-containing CA cases⁵⁻⁸ and it is likely to be reasonable in consideration of the relatively low oxidation state of silver cation. These weak interactions were corroborated by simple elution experiments through UV/Vis spectroscopic analysis; about 95% silver compounds are found to be extracted out from CA matrix in water at room temperature.

In this context, the glass transition temperature (T_g) of the films is expected to decrease as Ag metal concentration increases since the incorporated metal compounds act like plasticizers or impurities and increase the mobility of the polymer molecules, resulting in decrease in T_g . However, on the contrary to the expectation, the T_g of [CA-Ag] films increases about $40\text{ }^\circ\text{C}$ compared with that ($135.3\text{ }^\circ\text{C}$) of pure CA, and this result suggests that the incorporated silver compounds act as cross-linking reagents at higher temperature. This observation is believed to arise from the thermal decomposition of AgNO_3 in CA. Silver nitrate is well known to decompose at $414\text{ }^\circ\text{C}$ by following reaction:



But surprisingly, in [CA-Ag] films, the onset of decomposition is about $100\text{ }^\circ\text{C}$ in vacuum or in inert gas like CO_2 or N_2 . At $150\text{ }^\circ\text{C}$, all of silver cations in CA are reduced to metallic silver, yielding NO_2 gas as a major product and the pale brown color of the transparent [CA-Ag] films changes to silvery one with black tint after thermal reduction. At this stage, it is not clear why and how they decompose at such a low temperature, but the high dispersion of AgNO_3 in CA matrix is believed to be among the most probable reasons. The degree of those thermal reductions can be easily measured in infrared spectra by monitoring the intensity of the characteristic band due to nitrate at 817 cm^{-1} .

During the thermal reduction process, there are new bands at 2176 , 1670 , 1610 , 1580 , and 790 cm^{-1} in the infrared

spectra of the films, which are quite analogous to these observed in Ag-ZSM-5,¹³ Ag- Al_2O_3 ,¹⁴ Cu-ZSM-5,¹⁵ and Ag foil¹⁶ systems. Considering major product in thermal reduction reaction, these bands are obviously related to NO_2 species and can be assigned on the basis of careful comparison with known results¹³⁻¹⁶ as below;

IR bands (cm^{-1})	assignments
2176	$\text{Ag}(\text{NO}_2^+)$
1676	$\text{Ag}(\text{NO}_2)$
1600	(NO_2) physically adsorbed
1580	bidentate nitrate
790	ONO bend

After thermal reduction at $150\text{ }^\circ\text{C}$ all the bands due to nitrate disappear completely and the IR spectra of [CA-Ag] films are just like those of pure CA. Thus, metallic silver clusters formed in CA are believed to act as a kind of cross-linking reagent, leading to an aforementioned increase in T_g .

Reactions of silver nitrate in CA with H_2 and O_2 gas.

When a [CA-Ag] film is treated with H_2 gas (100 torr to 150 psi), the pale brown color of the films starts to darken even at room temperature, indicating that there is reduction of silver nitrate, and at above $120\text{ }^\circ\text{C}$, complete reduction is confirmed by IR spectroscopy and transmission electron microscopy of the films; in case of 10 wt.% [CA-Ag] films, Ag metal particles of about 20-30 nm in diameter are made after reduction reaction with H_2 gas ($120\text{ }^\circ\text{C}$, 150 psi, 4 hr), as shown in Figure 1(a); in 20 wt.% [CA-Ag] film case, the metal particle sizes increase to 90-200 nm after reduction reaction with H_2 ($150\text{ }^\circ\text{C}$, 150 psi, 8 hrs) as shown in Figure 1(b), denoting that the size of metal particles can be controlled by adjusting metal concentration in polymer and/or reaction conditions.

In addition, there are clearly many bands in $1400\text{-}1200\text{ cm}^{-1}$ region which arise from the well-known AgNO_2 species.¹¹ They, However, are too complex to study since

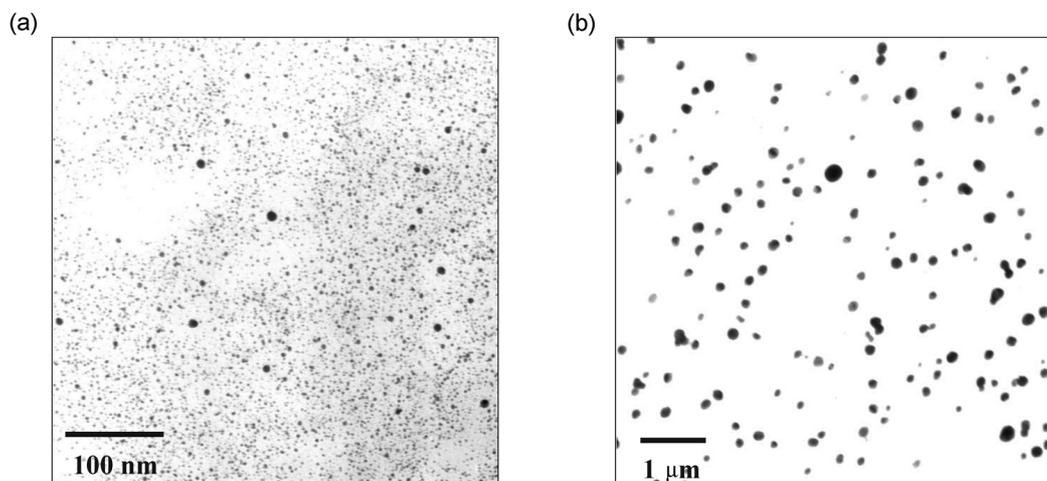


Figure 1. Transmission electron micrographs of (a) 10 wt.% [CA-Ag] films (b) 20 wt.% [CA-Ag] films after reduction reactions with H_2 gas at the described conditions.

these bands are coincided with many strong bands coming from cellulose acetate polymer molecules. Those bands due to nitro species in CA completely disappear after thermal reduction or reduction reaction with H₂ gas at over 120 °C. During the thermal reduction reaction process of untreated [CA-AgNO₃] films under O₂ gas, the same bands as above appear in the IR spectra of the films with higher intensities and no other bands are observed, confirming above assignments.

In case of reduction reaction of [CA-AgNO₃] films with H₂ gas, the intensities of above bands are very weak and after a 2 day reaction with H₂ (150 psi) at 150 °C, the gas products are easily identified to NH₃ and H₂O by gas phase IR spectroscopy. Accordingly, in this case, the nitrates in CA are assumed to be reduced via NO₂ intermediate and finally reduced to NH₃ by H₂ gas molecules. Oxidation of silver metal particles formed in CA is tried by treating them with excess oxygen gas (150 psi) at 150 °C for 4 days, but the silvery color of the films remain unchanged, and there are no infrared spectroscopic evidences¹⁷ for the formations of Ag₂O, AgO and AgO₂ species in CA at the described conditions.

Reaction of Ag in CA with CO, NO, and propylene gas.

Typical carbon monoxide species adsorbed on Ag (+1) was reported to show their infrared absorption bands in 2200-2151 cm⁻¹ region. But bulk Ag (0) carbonyls are unknown and surface Ag (0)-CO complexes are observed around 2060 cm⁻¹ only at the very low temperature.¹⁸ When 10 wt.% [CA-Ag] films are treated with CO gas (100psi) at room temperature, the color of the films remains unchanged and there are no infrared bands arising from silver carbonyl species in the films. Even at high temperature up to 150 °C, there is no appreciable change except the aforementioned thermal decomposition of silver nitrate.

Introduction of NO gas (50 torr) to 20 wt.% [CA-Ag] films with or without prior reduction reaction at 120-150 °C region leads to no infrared bands which can be attributed to silver nitrosyl complexes and this results reveals that the Ag⁺ ions in CA polymer matrix are not electrophilic enough to form silver nitrosyl complexes.¹⁹ However, the introduction of a 1 : 1 mixture of NO and O₂ gases to reduced [CA-Ag] films by H₂ gas at the similar conditions as above brings the appearance of many bands in their IR spectra; they are observed at 2176, 1676, 1607(sh), 1580(sh), and 790 cm⁻¹ in addition to complex bands in the 1400-1200 cm⁻¹ region, which are similar to those from the thermal decomposition under O₂ gas. But there are no evidences for N₂O₄, N₂O₃ species¹³ coordinated on the Ag⁺ cations or silver clusters in CA films.

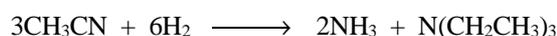
When 10 wt.% [CA-Ag] films are exposed to propylene gas (100 psi) at room temperature, two new bands at 1585 and 943 cm⁻¹ appear in their IR spectra and are easily attributed to $\nu(\text{C}=\text{C})$ from C=C bond coordinated to Ag(+1) and $\delta(\text{sp}^2\text{C}-\text{H})$ oop bend, respectively. In vacuum, they disappear completely and by repeated experiments, reversible coordination of propylene to Ag(+1) in CA is confirmed. This result is in good agreement with that of the

study for separation of propylene from propylene/propane mixture.¹⁹

Catalytic reactivity of Ag particles in CA. As previously discussed, silver nitrate compounds in CA are found to be easily reduced, resulting in the formation of silver nanoparticles with a relatively narrow size distribution. These small silver particles are expected to have various catalytic reactivity since silver is well known as an effective catalyst for the selective oxidation of ethylene or methanol in addition to the selective lean reduction of NO with propane and oxygen-containing compounds.²⁰ Therefore, in order to test the catalytic possibility of the [CA-Ag] films, following reactions are tried in a simple static state. All the reactions are performed with a catalytic amount of [CA-Ag] films, reduced with H₂ gas (150 psi, 150 °C, 2 days) using round bottom glass flasks or Parr reactors. Each reaction process is carefully monitored by gas phase FT-IR spectroscopy.

Hydrogenation of ethylene, benzene, styrene monomer and acetonitrile. A mixture of Ethylene and hydrogen gas (total pressure 150 psi) is reacted with 0.2 g of reduced [CA-Ag] films at 150 °C and after a 2 day reaction, all ethylene is confirmed to be converted to ethane by gas phase FT-IR spectroscopy and its turnover number is calculated to 46.23 (unit: number of substrate molecules transformed per Ag metal particles per hour). Similar gas phase reactions with benzene are tried with various gas mixture ratios (benzene: hydrogen = 1 : 1, 1 : 2, 1 : 5), but their products are easily identified to be only a mixture of cyclohexane and unreacted benzene molecules, and there are no evidences for cyclohexene and 1,3 or 1,4 cyclohexadienes, showing the typical characteristics of heterogeneous catalytic reactions without any selectivity. For comparison, analogous reactions with styrene monomer are carried out, but, interestingly, the product is identified to be ethyl benzene even in the reaction with excess hydrogen over a long reaction period; in this case, there is no hydrogenation of benzene ring at all. The reason is not clear at this stage, but it might be reasonable to assume that the steric hindrance of ethyl moiety blocks their approaches to silver active sites in CA.

In the case of hydrogenation of acetonitrile, product is likely to be ethylamine. However, when a 1 : 2 gas mixture of acetonitrile and hydrogen gases in mole ratio (total pressure: 150 psi) is reacted for 3 days at 150 °C, about 50% of acetonitrile is found to be converted to NH₃ and, surprisingly, triethylamine with a small amount of ethene by gas phase FT-IR and GC/Mass spectroscopy. The triethylamine is identified by its typical mass fragment pattern (EI-MS m/z 101, 100, 87, 86, 58, 56). Although precise quantitative analysis is not performed yet, the formation of triethylamine is quite interesting and attention is called here to this result since analogous one was already reported in the reduction reaction of acetonitrile with Pd or Pt catalysts²¹ as below:



But the reaction mechanism is not known yet and it is worthy to note that in the similar reaction using [CA-Cu]

films as catalysts, the product was reported to be ethylamine.⁵

Reduction of NO with H₂ gas. For the reduction of NO gas, a mixture of NO and excess hydrogen gas (total pressure: 150 psi) is reacted with 0.2 g of reduced 20 wt.% [CA-Ag] films at 150 °C. After a one day reaction, all NO gas is converted to NH₃ as below:



Similar reactions with excess CO gas are tried, but they are quite slow and only a small amount of NO gas is converted as below:



After these catalytic reactions, the [CA-Ag] films are carefully examined to find any coordinated species on silver reaction site in CA that might provide mechanistic information for each reaction. But, unfortunately, there are no any infrared spectral evidences for them in their spectra.

Thus, silver nitrate has been directly incorporated into CA films as a dispersion medium. The resulting homogeneous films of 5-20 wt.% silver metal complex concentration are found to be thermally stable up to 200 °C. During the thermal heating process, silver nitrate compounds start to decompose at about 100 °C in vacuum and at 150 °C, they are completely decomposed and this decomposition temperature of AgNO₃ in CA is quite low in comparison with that of free AgNO₃. Such thermal decomposition or reduction reaction with H₂ gas gives rise to silver metal nanoparticles in CA in a size range of 20-200 nm with relatively narrow size distributions and their sizes are found to be controlled by adjusting metal concentration in CA and/or the reaction conditions. These small silver metal particles in CA show various interesting catalytic reactivity in hydrogenation of olefins and acetonitrile, and NO reduction with H₂ gas. But unfortunately, the silver particles in CA are found to be inactive for the typical catalytic reaction of silver such as oxidation of ethylene or methanol. Further studies on the catalytic reaction using [CA-Ag] films in detail and their applications to reactive membrane are in progress.

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