

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

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Copper complexes have been directly incorporated into cellulose acetate (CA) and the resulting light blue colored homogeneous films of 5-20 wt.% copper acetate complex concentrations are found to be thermally stable up to 200 °C. The reaction chemistry of Cu in CA has been investigated by reacting them with small gas molecules such as CO, H₂, D₂, O₂, NO, and olefins in the temperature range of 25-160 °C, and various Cu-hydride, -carbonyl, -nitrosyl, and olefin species coordinated to Cu sites in CA are characterized by IR and UV/Vis spectroscopic study. The reduction of Cu(II) complexes by reacting with H₂ gas at the described conditions results in the formation of Cu₂O and copper metal nanoparticles in CA, and their sizes in 30-120 nm range are found to be controlled by adjusting metal complex concentration in CA and/or the reduction reaction conditions. These small copper metal particles show various catalytic reactivity in hydrogenation of olefins and CH₃CN; CO oxidation; and NO reduction reactions under relatively mild conditions.

Keywords : Copper nanoparticles in cellulose acetate polymer, Polymer-supported catalysis.

Introduction

Recently, inorganic, organic-polymer composite materials have been an active research field of particular interest because of their novel electronic, optical, magnetic, and physicochemical properties.¹⁻³ Also, these materials have received much attention for the preparations of inorganic nanoparticles in various organic polymers, which were reported to have relatively better control over nanometal cluster formations.⁴ Those nanoparticles in polymer or inorganic oxide matrices (nanocomposites) showed a variety of useful potential applications in ethylene-ethane gas separation or in catalysis.^{5,6} We reported about the preparations of Rh, Ru, Pd and Fe metal nanoparticles formed in various polymers such as cellulose acetate, polycarbonate, and polysulfone in addition to their reaction chemistry⁶⁻⁸; The transition metal particles in nanoscale or metal complexes in polymer matrices show quite interesting chemical and catalytic reactivity toward various small gas molecules under relatively mild conditions that are different from those of the corresponding free transition metal complexes, or from those in inorganic oxide-supported systems.⁹ In addition, it is noteworthy that the host polymer matrix itself significantly affects on the formation of nanometal particles and their reaction chemistry in the polymer.⁸

However, there have been only a few systematic comparative studies on these subjects. Continuing this line of works, we have incorporated copper metal complexes such as CuCl₂ and Cu(OAc)₂ into cellulose acetate and resulting Cu-containing polymer films have been investigated to understand the interactions between the Cu complexes and cellulose acetate molecules, the formation of Cu metal particles, and their reaction chemistry in the polymer host.

Experimental Section

Pure cellulose acetate(CA) and copper-containing CA

films (metal complex concentration: 5-20 wt.%) were prepared as previously reported,^{6,9} using cellulose acetate, CuCl₂, Cu(OAc)₂(Aldrich), and tetrahydrofuran or 2-methoxyethanol (Hayashi Pure Chemical Ind.) as a cosolvent. For a typical preparation of 10 wt.% copper acetate-containing CA films (designated as 10 wt.%[CA-Cu] film), 3.6 g of cellulose acetate and 0.4 g of Cu-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 20-90 μm, 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.¹⁰ The [CA-Cu] films containing CuCl₂ or Cu(OAc)₂ are light blue 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 including elution tests were recorded on 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 copper metal particles in CA. The gas products were quantitatively analyzed by Donam G/C 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 copper acetate-containing

CA films, there are several characteristic bands due to copper acetate complexes^{10c} at 3500, 2980, 1578, 1414, 1050, 1039, 690, and 635 cm^{-1} as well as the bands from CA. These bands from copper acetate complexes increase in their intensities as the metal complex concentration increases. In the case of $\text{Cu}(\text{NO}_3)_2$ -containing CA films, relatively electro-positive Cu(II) cations were reported to strongly interact with the oxygen atoms of the acyl groups in CA, and this was evidenced by infrared spectroscopic and thermal analysis studies.¹¹ Quite similar result is observed in CuCl_2 -containing CA films. However, in $\text{Cu}(\text{OAc})_2$ -containing CA films, there are no changes in the positions of the copper acetate bands after the metal complexes are incorporated into CA. This result means that the structure of copper acetate, which is usually a dimer, remains unchanged in CA polymer matrix. Therefore, it is believed that there is no significant direct interactions between copper complexes and CA molecules at this stage, and this is easily confirmed by simple elution test with UV/Vis spectroscopic analysis; When 10 wt.%[CA-Cu] films are immersed in water, about 73% of copper complexes in CA is extracted out from the CA matrix, as expected.

Meanwhile, the glass transition temperature (T_g) of the films is expected to decrease as Cu-metal complex concentration increase if there are no appreciable interactions between metal complexes and polymer molecules; usually in such case the incorporated metal complexes act like plasticizers in polymer which increase the mobility of polymer molecules, leading to a decrease in T_g . However, on the contrary to such expectation, the T_g of 10 wt.%[CA-Cu] film increases 41.5 $^\circ\text{C}$ compared to pure CA films (T_g ; 158.4 $^\circ\text{C}$), and this suggests that the incorporated metal complexes act as cross linking agents, leading to an increase in T_g .^{6,9,12} This result can be explained by the easy thermal decomposition of copper acetate complex in CA. The copper acetate complexes in solid state are well known to thermally decompose at 240 $^\circ\text{C}$ and to be reduced to Cu_2O and $\text{Cu}(\text{OAc})$, yielding CH_3COOH and CO_2 .¹³ In [CA-Cu] films, the onset of decomposition is about 80 $^\circ\text{C}$ in vacuum and the color of films changed from light blue to brown, which is the characteristic color of Cu_2O . Also, the intensities of the two distinctive bands at 1578 and 1414 cm^{-1} arising from the bridging acetate ligands, significantly decrease and the band at 1578 cm^{-1} shifts to lower frequency 1565 cm^{-1} , revealing that $\text{Cu}(\text{OAc})$ species in addition to Cu_2O are formed in CA during the decomposition process.¹³ But thermogravimetric analyses show that there is no appreciable mass loss below 200 $^\circ\text{C}$ except dehydration. Thus, in this thermal decomposition process, the dimeric copper acetate complexes are broken to mostly Cu_2O and $\text{Cu}(\text{OAc})$ without any major evolution of gas molecules, and consequently, the electron rich oxygen atoms of the acyl group of CA become able to interact with the Cu(II) species in CA, resulting in the aforementioned increases in T_g .

Reactions of copper acetate complexes in CA with H_2 and O_2 gas. When a [CA-Cu] film is treated with H_2 gas (150 psi) at 150 $^\circ\text{C}$ for four days, the color of the film

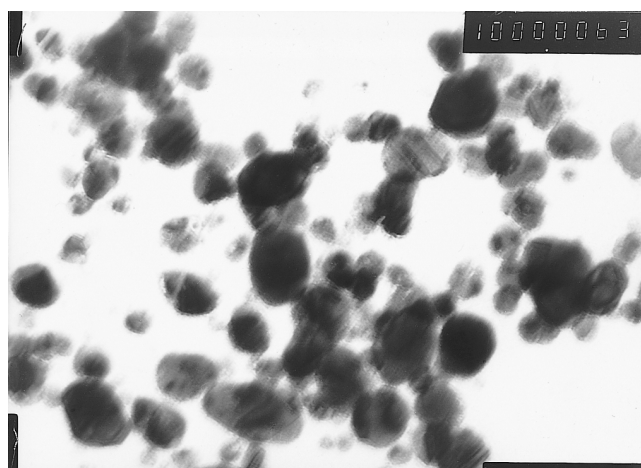


Figure 1. Transmission electron micrograph, showing Cu nanoparticles of 30-100 nm in diameter in a cellulose acetate film.

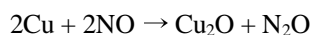
changes from light blue to black with purple or brown tint, and in their infrared spectra, all bands due to acetate ligands disappear completely, showing that there is a reduction reaction of $\text{Cu}(\text{II})$ ^{5b,c} in CA. Such reduction is confirmed by transmission electron microscopes of the films; in the case of 10 wt.%[CA-Cu] film, Cu metal particles of about 30-100 nm in diameter are produced after reduction reaction (shown in Figure 1); in 20 wt.%[CA-Cu] films, the metal particle sizes increase to 50-120 nm, denoting that the size of metal particles can be controlled by adjusting the metal concentration in the polymer. In other set of experiments, it is found that the metal particle size can be also controlled by reduction conditions like reduction temperature and/or reaction time. In addition, there is a new weak IR band at 1520 cm^{-1} after reduction reaction, and this band is stable in air, but slowly disappears after reaction with O_2 or NO gas. In order to ascertain the origin of this band, the [CA-Cu] films are treated with D_2 gas under the same conditions as above, but it is very difficult to find the corresponding $\nu(\text{Cu-D})$ band because of strong bands due to CA at first sight. In their subtraction spectra, a weak band at 900 cm^{-1} is found. Accordingly, this band at 1520 cm^{-1} is assigned to bridging copper hydride stretching band.

In the UV/Vis spectra of blue colored [CA-Cu] films, there is a broad band at 700 nm with a charge transfer band below 400 nm. When these films are treated with H_2 gas as above, a new strong band at 576 nm appears and this result is quite analogous to those of the thermal decomposition experiments, indicating that the reaction at the conditions gives rise to the formation of Cu_2O in addition to copper(0) metal particles in CA. It is very hard to pinpoint corresponding IR band due to Cu_2O at 620 cm^{-1} ^{10b} since CA has a strong absorption band at 610 cm^{-1} . But after a series of consecutive reactions of the [CA-Cu] films using H_2 and O_2 gas in addition to the careful subtraction IR spectroscopic study, the band at 620 cm^{-1} is identified after reduction reaction with H_2 gas. For further reduction of Cu(I) species to Cu(0), the [CA-Cu] films are treated with H_2 gas (160 psi) at 160

°C for a week, but the films become quite brittle and so, the complete reduction is unsuccessful.

When the black [CA-Cu] films reduced with H₂ gas as previously described are consecutively treated O₂ gas (150 psi) at 150 °C for 2 days, the color of the films changes to yellowish green and the band at 1520 cm⁻¹ disappears in their IR spectra, while new bands at 910, 890, 850, and 620 cm⁻¹ appear in their subtraction IR spectra. On the basis of known IR data, these new bands are believed to arise from the end-on, or bridging Cu-peroxide species^{10c}, and aforementioned Cu₂O species. But, surprisingly, there is no evidence for the black colored CuO which is a typical product from the oxidation reaction of Cu(I) or Cu(0) species.^{5b,c} In UV/Vis spectra, only a strong charge transfer band below 400 nm is observed with a shoulder band near 576 nm. At this stage, the origin of the CT band is not clear. Thus, it is concluded that the dimeric Cu(II) acetate complexes in CA can be chemically reduced to Cu₂O and Cu(0) species and reoxidized to Cu₂O and CuO₂ by reaction with O₂ gas at the described conditions. When these reduced films are left in air for long time (more than a week), the Cu(0) metal atoms and Cu₂O in CA are transformed to the green-colored basic carbonate [CuCO₃ · Cu(OH)₂], which can be easily identified by its IR^{10b} and UV/Vis spectra.

Reactions of Cu in CA with NO gas. When a 10 wt.% [CA-Cu] film reduced with H₂ gas (150 psi) at 150 °C for a day is exposed to NO gas under the same condition, the color of the film changes to brown from dark black and two bands appear at 2170 and 1590 cm⁻¹ in its IR spectrum. This result indicates that the copper metals are oxidized to brown colored Cu₂O while nitric oxides are reduced to N₂O¹⁴ as below;



The band at 2170 cm⁻¹ is thought to correspond N₂O gas molecules coordinated on Cu complexes since free N₂O gas molecule shows a strong IR band at 2236 cm⁻¹. Quite analogous experimental result was reported in the IR study on the surface reaction of NO gas absorbed on copper ion-exchanged ZSM-5 zeolites.¹⁵ But it should be noted that in our case, the Cu(NO)₂ species which is an important intermediate in the reaction is not observed. The band at 1590 cm⁻¹ is in low frequency region compared to those of known transition metal nitrosyl complexes, indicating that it arises from the bridged nitrosyl species in Cu metal atoms. Upon similar reaction without prior reduction reaction as above, additional weak infrared bands are detected below 1500 cm⁻¹, but they are not clear because of the intense bands due to the cellulose acetate molecules.

Reactions of Cu in CA with CO gas. When 10 wt.% [CA-Cu] films are treated with CO gas (150 psi) at 150 °C, the color of the films changes to brown and there are no carbonyl bands in their infrared spectra. Therefore, under these conditions, this seems to be no reactions at all except the thermal decomposition of copper complexes and dehydration as discussed in earlier section. However, when the [CA-Cu] films with prior reduction reaction with H₂ gas are reacted with CO gas at the same conditions as above, two

weak bands at 2060 and 1630 cm⁻¹ appear in their IR spectra. The band at 2060 cm⁻¹ can be easily assigned to terminal copper(I) carbonyl species, compared to the known infrared data for transition metal carbonyl compounds.^{16a} The origin of the other band at 1630 cm⁻¹ is not clear since bridged copper carbonyls typically appear at around 1900 cm⁻¹. But some unusual semitriple bridging carbonyl groups exhibit ν(CO) band around 1600 cm⁻¹ region. Accordingly, this low ν(CO) band is tentatively assigned to a semitriple bridging carbonyl stretching vibration.^{10c}

Reaction with Cu in CA with propene. Recently, the interaction between copper(I) complexes and olefins has been received much attention because it can be utilized for the olefin separation from the gas mixture of olefin and alkane.¹⁷ When the [CA-Cu] films reduced with H₂ gas (150 psi) at 150 °C for 3 days are treated with propene at the same conditions, two new bands at 1618 and 1590 cm⁻¹ appear in their IR spectra and are assigned to the propene molecules coordinated to different Cu(I) sites in CA. Compared to free ν(C=C) frequency at 1652 cm⁻¹, there seems to be appreciable back bonding between Cu(I) and propene molecules in CA. The frequencies of Cu-carbonyl, -hydride, -nitrosyl, and propene species formed in CA discussed here are listed as below;

IR frequencies	assignments
2060 cm ⁻¹	ν (CO), Cu(I)-CO terminal
1630 cm ⁻¹	ν (CO), Cu-CO semitriple bridged
2170 cm ⁻¹	ν (N ₂ O), Cu(I)-N ₂ O bridged
1590 cm ⁻¹	ν (NO), Cu-NO bridged
1520 cm ⁻¹	ν (Cu-H), Cu-H bridged
1618, 1590 cm ⁻¹	ν (C=C), coord. to Cu(I)

Catalytic reactivity of Cu in CA. As discussed in above sections, the Cu complexes in CA are found to be quite active toward CO, H₂, O₂, NO, and propene under relatively mild conditions. Also, copper nanoparticles are observed to be formed in CA by thermal heating or by reacting with H₂ gas, and they are expected to act as catalytic sites in CA. Therefore, in order to test the catalytic possibility, following reactions are tried in a simple static state. All the catalytic reactions are carried out with 20 wt.% [CA-Cu] films reduced by H₂ gas (150 psi, 150 for 2 days) using Parr reactors. Each reaction process is carefully monitored by gas phase FT-IR and quantitatively analyzed by G/C.

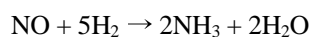
Hydrogenation of ethylene, benzene, styrene monomer, and acetonitrile. A 1 : 1 mixture of ethylene and hydrogen (total pressure 150 psi) is reacted with 0.2 g of reduced [CA-Cu] films at 150 °C, and after a 4 hours reaction, about 90% of ethylene is converted to ethane and its turnover number is calculated to 114.9 (unit: substrate molecules transformed per Cu metal particle per hour). When 3.39 mL of benzene is treated with H₂ gas (60 psi) at 150 °C and 0.2 g of reduced [CA-Cu] films for one day, only 10% of benzene is transformed to cyclohexane and there are no evidences for the formations of cyclohexadiene or cyclohexene. In other experiments, different amounts of hydrogen gas are tried, but the product is only cyclohexane, which is a typical heterogeneous catalytic reaction product without any selectivity.

Similarly, hydrogenation of styrene monomer (8.70 mL) is performed under the same conditions as above and after a one day reaction, about 75% of reactant is transformed to ethylbenzene. Although excess hydrogen is tried at 160 °C, but there are no formations of ethylcyclohexane and ethylcyclohexenes in the products. Also, hydrogenation of acetonitrile (2.64 mL) is tried with hydrogen gas (70 psi) and 0.2 g of reduced 20 wt.%[CA-Cu] films. When this mixture is heated to 150 °C, the total pressure becomes 150 psi and after a one day reaction, about 80% of substrate molecules is transformed into ethylamine.

Oxidation of CO by O₂ gas. A 1 : 1 mixture of CO and O₂ gas (total pressure : 100 psi) with 0.2 g of [CA-Cu] films is heated to 150 °C and at this temperature, total gas pressure become 150 psi. After a one-day reaction, about 80% of CO gas is converted to CO₂ gas.

Reduction of acetone with H₂ gas. 5.51 mL of acetone is heated with H₂ gas (50 psi) and 0.2 g of reduced 20 wt.% [CA-Cu] films to 150 °C and at this temperature total gas pressure becomes 150 psi. After a three-day reaction, about 80% of acetone is converted to 2-propanol.

Reduction of NO gas with H₂ or CO gas. For the reduction of NO gas, a mixture of NO (30 psi) and H₂ gas (70 psi) is reacted with 0.2 g of reduced 20 wt.%[CA-Cu] films and heated to 150 °C. After a one-day reaction, about 75% of NO gas is converted to N₂O and H₂O. But similar reaction with excess hydrogen gas (about 5 times excess than stoichiometric equivalent) under the same conditions results in the formation of NH₃ rather than N₂O gas as below;



The NO reduction reaction with CO gas is analogously tried as above and after a one-day reaction, about 60% NO gas is converted to N₂O gas and the products of this reaction (N₂O and CO₂ gas) are independent to the CO gas pressure and reaction conditions. The possibility of NO reduction to N₂ gas is carefully examined but fails. The [CA-Cu] films used in this experiment is investigated to get mechanistic information, but their IR spectra shows only the two bands at 2170 and 1590 cm⁻¹ discussed in early section; There are no evidences for the typical NO dissociation intermediates such as Cu-isocyanide, -cyanide, hyponitrite, Cu(NO)₂, and CuH-(NO)₂ species.^{15,18} Therefore, it is believed that the direct attacks of H₂ or CO gas molecules to the coordinated nitrosyl groups on Cu metal sites in CA are involved in the reduction pathway.

Conclusions

Copper complexes have been directly incorporated into CA and the resulting light blue colored homogeneous films of 5-20 wt.% copper acetate complex concentrations are found to be thermally stable up to 200 °C. During the thermal heating process, copper acetate complexes are decomposed to mostly Cu₂O and copper(I) acetate species

but below 200 °C, there is almost no loss in mass of the films due to the copper complex decomposition, except dehydration. The reaction chemistry of Cu in CA has been investigated by reacting them with small gas molecules such as CO, H₂, D₂, O₂, NO, and olefins in the temperature range of 25-160 °C, and various Cu-hydride, -carbonyl, -nitrosyl, and olefin species coordinated to Cu sites in CA are characterized by IR and UV/Vis spectroscopic study. The reduction process of Cu(II) complexes to Cu₂O and copper metal nanoparticles by reacting with H₂ gas at the described conditions is discussed and the sizes of copper metal particles in 30-120 nm range are found to be controlled by adjusting metal complex concentration in CA and/or the reduction reaction conditions. These small copper metal particles show various catalytic reactivity in hydrogenation of olefins and CH₃CN; CO oxidation; and NO reduction reactions under relatively mild conditions.

References

1. El-Sall, M. S.; Slack, W. *Macromolecules* **1995**, *28*, 8456.
2. Golden, J. H.; Deng, H.; DiSalvo, F. J.; Frechet, J. M. J.; Thompson, P. M. *Science* **1995**, *268*, 1463.
3. Martin, C. R. *Chem. Mater.* **1996**, 1739.
4. Sohn, B. H.; Cohen, R. E. *Acta polymer* **1996**, *47*, 340.
5. (a) Regar, T. S.; Janda, K. D. *J. Am. Chem. Soc.* **2000**, *122*, 6929. (b) Lin, Y. S.; Ji, W.; Wang, Y.; Higgins, R. J. *Ind. Eng. Chem. Res.* **1999**, *38*, 2292. (c) Terry, K. W.; Lugmair, C. G.; Gantzel, P. K.; Tilley, T. D. *Chem. Mater.* **1996**, *8*, 274.
6. Shim, I. W.; Oh, W. S.; Jeong, H. C.; Seok, W. K. *Macromolecules* **1996**, *29*, 1099.
7. Shim, I. W.; Kim, J. Y.; Kim, D. Y.; Choi, S. *Reactive and Functional Polymers* **2000**, *43*, 71.
8. Shim, I. W.; Choi, S.; Noh, W. T.; Kwon, J.; Cho, J. Y.; Chae, D. Y.; Kim, K. S. *Bull. Korean Chem. Soc.* **2001**, *22*, 772.
9. Shim, I. W.; Kim, D. Y.; Choi, S.; Kong, K. H.; Choe, J. I. *Reactive and Functional Polymers* **2000**, *43*, 287 and references therein.
10. (a) Pouchet, C. J. *The Aldrich Library of FT-IR Vapor Phase*, 1st Ed.; Aldrich Chemical Company, Inc.: Milwaukee, Wisconsin, U. S. A., 1983; Volume 3. (b) Nyquist, R. A.; Kagel, R. O. *Infrared Spectra of Inorganic Compounds* (3800-45 cm⁻¹); Academic Press: New York, U. S. A., 1977; Vol. 4. (c) Nakamoto, K. *Infrared and Raman Spectra of Inorganic and Coordination Compounds*, Part A&B, 5th Ed.; John Wiley & Sons, Inc.: New York, U. S. A., 1997.
11. Barbucci, R.; Casolaro, M.; Corezzi, S.; Reginato, G. *Polymer* **1986**, *27*, 1986.
12. Drzewinski, M.; Macknight, W. J. *J. Appl. Polym. Sci.* **1985**, *30*, 4735.
13. *Inorganic Syntheses*; Allcock, H. R., Ed. in Chief; John Wiley & Sons, Inc.: New York, U. S. A., 1980; Vol. 20, p 53.
14. McNeill, K.; Bergman, R. G. *J. Am. Chem. Soc.* **1999**, *121*, 8260.
15. Iwamoto, M.; Yahiro, H.; Mizuno, N.; Zhang, W. X.; Mine, Y.; Furukawa, H.; Kagawa, S. *J. Phys. Chem.* **1992**, *96*, 9360.
16. (a) *Comprehensive Coordination Chemistry*; Wilkinson, G. FRS. Ed. in Chief; Pergamon Press: Oxford, U. K., 1987; Vol. 5, p 566, and references therein. (b) *Encyclopedia of Inorganic Chemistry*; Bruce King, R., Ed. in Chief; John Wiley & Sons, Inc.: New York, U. S. A., 1994; Vol. 2, p 822 and references therein.
17. Safarik, D. J.; Eldridge, R. B. *Ind. Eng. Chem. Res.* **1998**, *37*, 2571.
18. Kudo, A.; Steinbery, M.; Bard, A. J.; Campion, A.; Fox, M. A.; Mallowk, T. E.; Webber, S. E.; White, J. M. *J. Catal.* **1990**, *125*, 565.