Magnetic field effect on gas-phase synthesis of metal-containing ultrafine particles from iron pentacarbonyl and carbon disulfide

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Abstract

From a gaseous mixture of Fe(CO)5 and CS2, sedimentary aerosol particles involving organometal compounds were produced under UV light irradiation at 313 nm. Chemical composition of the sedimentary aerosol particles was controlled by a magnetic field and by post-exposure with UV light. By applying a magnetic field up to 5 T, photochemical reactivity of Fe(CO)5 molecules was promoted and the amount of chemical species originating from Fe(CO)5 increased with increasing magnetic field. By irradiating UV light upon the deposited particles, solid-state photochemical reactions took place in the particles, and CO groups bonded to Fe atom were effectively evolved from the sedimentary aerosol particles. These methods can be utilized to modify chemical composition of the metal-containing sedimentary particles.

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1. Introduction

Ultrafine and nano-size particles involving metal clusters can be used as a building block of nanowires and nanodevices in addition to digital dots in high density recording materials. Synthesis of metal nanoparticles in the gas phase has been done by irradiating IR laser light on SF6-sensitized gaseous iron pentacarbonyl (Fe(CO)5), resulting in production of nanoparticles of metal iron of 10 nm in size [1]. Nanoparticles and ultrafine particles can also be produced from the gaseous molecules using photochemical reactions of organic molecules such as acrolein [2] and carbon disulfide (CS2) [3]. In the present paper, photochemical reactions of a gaseous Fe(CO)5 and CS2 mixture have been employed to produce ultrafine particles. Photochemical reactions between these molecules are expected to produce novel chemical species involving organometal complexes and to afford the particles novel chemical structures and properties [4].

Chemical structure of the ultrafine particles can be controlled by two ways in the photochemical method under study. One method is to irradiate UV light on the sedimentary particles already deposited on a substrate in order to initiate solid-state photochemical reactions in the particles (post-exposure with UV light) [5], and the other method is to apply a magnetic field during photochemical reactions. It has been found recently by us that magnetic field influences photochemical reactions of some gaseous mixtures during the formation of aerosol particles, resulting in the change in chemical composition of the sedimentary aerosol particles [6–9]. Both methods have been applied to photochemical synthesis of the ultrafine particles from a gaseous mixture of Fe(CO)5 and CS2, and the change of chemical composition has been studied from the analysis of FT-IR spectra.

2. Experimental

Fe(CO)5 (Kanto, 95%) and CS2 (Kanto, 98%) were degassed by freeze-pump-thaw cycles in the dark and purified by vacuum distillation immediately before use. To prepare a gaseous mixture, each vapor was introduced successively into a cylindrical Pyrex cell (inner diameter 35 mm, length 160 mm, volume 154 cm3) or a small cylindrical Pyrex cell (inner diameter 20 mm, length 160 mm, volume 50 cm3) equipped with a couple of quartz windows through a vacuum line equipped with a capacitance...
manometer (Edwards Barocel Type 600). The background pressure of the irradiation cell was less than \(8 \times 10^{-5}\) Torr (1 Torr = 133.3 Pa). The partial pressures of Fe(CO)\(_5\) and CS\(_2\) in the irradiation cell were determined from FT-IR band intensities. The gaseous samples were irradiated with a medium pressure mercury lamp (Ushio UM-452, 450W) through a UV29 (or UV31) and a UV33S filters (energy, 8.0 (or 3.5) mJ/s cm\(^2\)) to excite both Fe(CO)\(_5\) and CS\(_2\) molecules at 313 nm, although Fe(CO)\(_5\) was excited more (\(\approx 50\) times) efficiently than CS\(_2\). The aerosol particles were deposited on a glass and/or Cu substrates accommodated in the irradiation cell. Scanning electron microscope (SEM) images were taken with a JEOL JSM 6060 scanning electron microscope. Sedimentary aerosol particles were mixed with KBr powder to prepare KBr pellets and FT-IR spectra of the sedimentary particles in the pellets were measured with a Nicolet NEXUS 470 FT-IR spectrometer. Light intensity scattered perpendicularly to the incident monitor (He–Ne laser) light by the aerosol particles as formed in the irradiation cell under UV light irradiation was measured through a Y-52 filter with a combination of a photomultiplier tube (EMI 6256S) and a lock-in amplifier (SRS SR-530). Magnetic field was applied by a helium-free superconducting magnet (Toshiba TM-5SP) to study the magnetic field effect on chemical processes.

3. Results and discussion

Under UV light irradiation at 313 nm for 10 min, pure Fe(CO)\(_5\) vapor (1.0 Torr) produced two kinds of morphologically different deposits, i.e. hexagonal rod with a mean size of \(2.8 \times 2.4\) \(\mu\)m and crystalline particles with a mean size of 0.46 \(\mu\)m (Fig. 1). On the other hand, a gaseous mixture of Fe(CO)\(_5\) (1.1 Torr) and CS\(_2\) (2.0 Torr) produced spherical sedimentary aerosol particles with a mean diameter of 0.28 \(\mu\)m, although pure CS\(_2\) vapor at a pressure of 2 Torr did not produce any deposits \([10–14]\). The morphological change of the deposits from the gaseous mixture clearly showed that CS\(_2\) molecules were incorporated into the photochemical reactions of Fe(CO)\(_5\).

FT-IR spectrum of the sedimentary aerosol particles produced from a gaseous mixture of Fe(CO)\(_5\) (1.1 Torr) and CS\(_2\) (2.0 Torr) is shown in Fig. 2, compared with the spectra of deposits produced from pure Fe(CO)\(_5\) vapor (1.0 Torr) and from pure CS\(_2\) vapor (50 Torr). The FT-IR spectrum of deposits from pure Fe(CO)\(_5\) vapor (Fig. 2a) showed the bands characteristic of C–O and C=C=O stretching vibrations at 1825 and 2015 cm\(^{-1}\), showing that the major chemical species of the deposits was Fe\(_2\)(CO)\(_9\) \([15,16]\), in addition to a slight amount of Fe\(_3\)(CO)\(_{12}\) \([17]\). On the other hand, FT-IR spectrum of the sedimentary aerosol particles deposited from the gaseous mixture (Fig. 2c) exhibited only C=O stretching bands at 2009, 2038, and 2080 cm\(^{-1}\), indicating that Fe–(C=O)–Fe chemical bond was not formed by the incorporation of CS\(_2\) molecules. In addition, FT-IR bands observed with the sedimentary aerosol particles produced from pure CS\(_2\) vapor (Fig. 2b) \([18–23]\) almost disappeared in Fig. 2c, supporting that the bond formation between Fe(CO)\(_4\) species \([24]\) and CS\(_2\) molecules is the primary chemical reaction of the gaseous mixture.

The nucleation and propagation processes during aerosol particle formation were monitored by measuring the He–Ne laser light intensity scattered by the aerosol particles which were formed under UV light irradiation. The results are shown in Fig. 3. Compared to the case of pure Fe(CO)\(_5\) vapor (1.0 Torr) where the nucleation and propagation reactions were fast and the scattered light was detected only for the first 1 min, scattered light was detected for the first 10 min for the gaseous mixture of Fe(CO)\(_5\) and CS\(_2\) molecules, showing that aerosol particles were actually formed by the chemical reaction between Fe(CO)\(_5\) and CS\(_2\) molecules. Incorporation of CS\(_2\) molecules interrupted the formation of Fe\(_2\)(CO)\(_9\) by making Fe–S bond.

Chemical processes in the gaseous phase were investigated by measuring FT-IR spectrum of a gaseous mixture of Fe(CO)\(_5\) (1.1 Torr) and CS\(_2\) (2.0 Torr). The spectrum of the mixture before light irradiation coincided with the
superimposed spectra of the individual Fe(CO)₅ and CS₂ (Fig. 4A), showing the absence of chemical reaction and complex formation between the components. Upon UV light exposure, the spectrum of the gaseous mixture was measured after allowing for complete sedimentation of the formed aerosol particles. Rate of depletion of δ(Fe–C–O) band at 645 cm⁻¹ of Fe(CO)₅ [25,26] was compared between in pure Fe(CO)₅ vapor and in the gaseous mixture (Fig. 4B). Gaseous Fe(CO)₅ molecules were almost consumed in 10 min in pure Fe(CO)₅ vapor and in 25 min in the gaseous mixture. The value, (−ln A/A₀) was plotted against cumulative irradiation time, and the depletion rate of Fe(CO)₅ (assuming the pseudo first order decay) was determined to be 3.5 ± 10⁻³ s⁻¹ in the gaseous mixture and 7.8 ± 10⁻³ s⁻¹ for pure Fe(CO)₅ vapor. Depletion of Fe(CO)₅ molecules was decelerated by ≈2 times due to the presence of CS₂. As to CS₂ molecules, the change in ν(C=S)
band intensity at 1530 cm\(^{-1}\) was not observed in pure CS\(_2\) vapor at a pressure of 2.0 Torr, but in the gaseous mixture, a slight decrease in the band intensity was detected. From the estimation of the number of molecules depleted over 10 min of UV light irradiation, molar ratio of depleted Fe(CO)\(_5\) and CS\(_2\) molecules was 5:1. Unfortunately, we found that the molar absorption coefficient of ν(C=S) band of CS\(_2\) molecules remaining in the gas phase was greatly influenced (i.e. increased) by the existence of CO molecules, which were evolved from Fe(CO)\(_5\) under light irradiation in the present experiment. Therefore, the number of depleted CS\(_2\) molecules evaluated from FT-IR spectral intensity was the minimum value of CS\(_2\) molecules incorporated into the chemical reaction.

To investigate magnetic field effect on both the particle size and the chemical structure, sedimentary aerosol particles were produced from a gaseous mixture of Fe(CO)\(_5\) (1.1 Torr) and CS\(_2\) (2.0 Torr) in a superconducting magnet under light irradiation at 313 nm. The particle size distribution was measured from SEM images of the sedimentary particles. Due to the limited space of the bore (inner diameter 60 mm) available in the superconducting magnet, a small cylindrical cell with inner diameter of 20 mm was used in this experiment. With decreasing diameter of the irradiation cell (from 35 to 20 mm), deposited particles became smaller and the mean diameter of the sedimentary particles reduced to 0.19 from 0.28 μm. This is due to a shorter propagation time of particle growth in a smaller irradiation cell [9]. The mean diameter of the sedimentary particles produced under magnetic fields of 3 and 5 T was 0.18 and 0.16 μm, respectively. The mean diameter decreased by ≈12% with the application of a magnetic field of 5 T.

FT-IR spectra of the sedimentary aerosol particles produced in a superconducting magnet are shown in Fig. 5. With increasing magnetic field up to 5 T, band intensities in the 2000 cm\(^{-1}\) region assigned to ν(C=O) increased accompanying a slight contribution of 1825 and 2016 cm\(^{-1}\) bands assignable to Fe\(_2\)(CO)\(_9\). The band intensity of δ(Fe–C–O) at 570 cm\(^{-1}\) also increased with increasing magnetic field. These results indicated that magnetic field promoted the chemical reactivity of Fe(CO)\(_5\) molecules, resulting in the increase in the amount of chemical species originating from Fe(CO)\(_5\).

The magnetic field effect on the chemical structure was further measured with a gaseous mixture with increased partial pressure of CS\(_2\). FT-IR spectra of the sedimentary aerosol particles produced from a gaseous mixture of Fe(CO)\(_5\) (0.9 Torr) and CS\(_2\) (21 Torr) are shown in Fig. 6. Compared to the spectrum in Fig. 5a, band intensities in the 800–1700 cm\(^{-1}\) region increased in the spectrum of the sedimentary particles produced without a magnetic field (Fig. 6a), showing that a greater amount of CS\(_2\) molecules were incorporated into the aerosol particles. From the depletion of FT-IR band intensity of the gaseous mixture, molar ratio of Fe(CO)\(_5\) and CS\(_2\) molecules depleted over 10 min of UV light irradiation was evaluated to be 3:1. Although this value was only the minimum amount of CS\(_2\) molecules incorporated into the chemical reaction, the result
clearly showed that a greater amount of CS$_2$ molecules was incorporated into the sedimentary particles when the partial pressure of CS$_2$ was increased. With increasing magnetic field up to 5 T, the C=O stretching band intensity in the 2000 cm$^{-1}$ region increased, indicating that chemical reactivity of Fe(CO)$_5$ was promoted under a magnetic field. However, we could not detect any contribution of Fe$_2$(CO)$_9$ species. This indicated that incorporation of a greater amount of CS$_2$ molecules was enough to interrupt the formation of Fe–(C=O)–Fe chemical bond necessary to form Fe$_2$(CO)$_9$ species even in the presence of a high magnetic field where chemical reactivity of Fe(CO)$_5$ was promoted.

Under UV light irradiation, electronically excited Fe(CO)$_5$ evolves one CO group to produce Fe(CO)$_4$ [24]. In pure Fe(CO)$_5$ vapor, Fe(CO)$_4$ reacts with Fe(CO)$_5$ to produce mainly Fe$_2$(CO)$_9$ (reaction (2)), but in the gaseous mixture of Fe(CO)$_5$ and CS$_2$, Fe(CO)$_4$ reacts promptly with CS$_2$ molecules to produce an intermediate species (Fe(CO)$_4$·CS$_2$) (reaction (3)), followed by further chemical reactions with Fe(CO)$_5$ and CS$_2$ molecules to produce aerosol particles (reaction (4)).

$$\text{Fe(CO)}_5 + hv \rightarrow \text{Fe(CO)}_4 + \text{CO} \quad (1)$$

$$\text{Fe(CO)}_4 + \text{Fe(CO)}_5 \rightarrow \text{Fe}_2(\text{CO})_9 \quad (2)$$

$$\text{Fe(CO)}_4 + \text{CS}_2 \rightarrow (\text{Fe(CO)}_4 \cdot \text{CS}_2) \quad (3)$$

$$(\text{Fe(CO)}_4 \cdot \text{CS}_2) + m\text{Fe(CO)}_5 + n\text{CS}_2$$

$$\rightarrow \text{aerosol particle formation} \quad (4)$$

Under a magnetic field, the intermediate species, (Fe(CO)$_4$·CS$_2$) favors the chemical reaction with Fe(CO)$_5$ molecules in reaction (4) as in Fe(CO)$_4$ in reaction (2), although the latter is a minor chemical reaction in aerosol particle formation. Between the chemical species of Fe(CO)$_5$, Fe(CO)$_4$, and Fe$_2$(CO)$_9$, only Fe (CO)$_4$ is paramagnetic [27]. This character may be related to the acceleration of chemical reactions of (2) and (4) under a magnetic field.

To study the effect of post-exposure with UV light on the chemical composition of the sedimentary particles, sedimentary particles were produced from a gaseous mixture of Fe(CO)$_5$ (1 Torr) and CS$_2$ (5 Torr) (a) before and (b) after post-exposure with UV light at 313 nm for 2 h.

![FT-IR spectra of sedimentary particles produced from a gaseous mixture of Fe(CO)$_5$ (1 Torr) and CS$_2$ (5 Torr) (a) before and (b) after post-exposure with UV light at 313 nm for 2 h.](image)

**Fig. 7.** FT-IR spectra of sedimentary particles produced from a gaseous mixture of Fe(CO)$_5$ (1 Torr) and CS$_2$ (5 Torr) (a) before and (b) after post-exposure with UV light at 313 nm for 2 h.

produced successfully under UV light irradiation at 313 nm. Under a magnetic field up to 5 T, photochemical reactivity of Fe(CO)$_5$ was promoted, and the amount of chemical species originating from Fe(CO)$_5$ increased with increasing magnetic field. By irradiating UV light upon the deposited particles, solid-state photochemical reactions took place in the particles, and CO group bonded to Fe atom was effectively evolved from the sedimentary aerosol particles. Both methods can be utilized to modify chemical composition of the metal-containing sedimentary particles.

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