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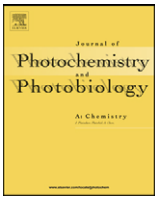

Photochemical synthesis of linearly aggregated fine particles from a ternary gaseous mixture involving iron pentacarbonyl

Hiroshi Morita[a,*], Kohsuke Abe[b], Masashi Takahashi[b]

[a] Graduate School of Advanced Integration Science, Chiba University, Yayoi-cho, Inage-ku, Chiba, Chiba 263-8522, Japan
[b] Graduate School of Science, Toho University, Miyama, Funabashi, Chiba 274-8510, Japan

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ABSTRACT

From a gaseous mixture of iron pentacarbonyl ($Fe(CO)_5$), allyltrimethylsilane (2-propenyltrimethylsilane) (ATMeSi), and carbon disulfide (CS_2), sedimentary aerosol particles with a mean diameter of 0.56 μm were produced under UV light irradiation with a medium pressure mercury lamp. Chemical structure of the sedimentary aerosol particles was investigated by measuring FT-IR and Raman spectra, and chemical composition, by measuring scanning electron microscopy/energy dispersive spectroscopy (SEM-EDS). From the analysis, it was strongly suggested that CS_2 reacted with $Fe(CO)_5$ to produce $Fe(CO)_4{-}S{-}C({=}S){-}Fe(CO)_4$ species by σ-coordination of CS_2 molecule, that two Fe atoms were bonded via carbon-bridging thiocarbonyls produced from CS_2, and that ATMeSi coordinated to Fe atom via π-coordination of allyl group of ATMeSi. Sedimentary aerosol particles produced under a magnetic field up to 5 T were found to increase their particle size, and chemical composition of the deposited particles was changed by the post-exposure with UV light by evolving volatile $Fe(CO)_n$ ($n = 1$–3) species in addition to CO groups bonded to Fe atom. During the sedimentation process of the aerosol particles, linearly aggregated particles (i.e., particle wires) were efficiently formed at the vicinity of the front edge of a glass plate placed at the bottom of the irradiation cell. Experimental details to form long particle wires were discussed briefly.

1. Introduction

Carbon disulfide (CS_2) reacts with transition metal complexes to exhibit π-CS_2 coordination, to form σ-bonded complex through a S atom, and to form complexes with bridging CS_2 group [1]. Iron pentacarbonyl ($Fe(CO)_5$) is a photoreactive transition metal complex, and under UV light irradiation a gaseous mixture of $Fe(CO)_5$ and CS_2 produced spherical aerosol particles [2,3]. Chemical analysis by scanning electron microscopy/energy dispersive spectroscopy (SEM-EDS) and FT-IR spectrum of the sedimentary aerosol particles strongly suggested that the major chemical structure was similar to the one of $Fe_2(CO)_9$ but two Fe atoms in the particles were connected by σ-coordinated bridging CS_2 [3].

$Fe(CO)_5$ can also react with vinylsilanes to form iron tetracarbonyl π-coordinated vinylsilanes [4]. From a gaseous mixture of $Fe(CO)_5$ and allyltrimethylsilane (2-propenyltrimethylsilane) (ATMeSi), crystalline deposits were produced under UV light irradiation in addition to a small amount of spherical aerosol particles [5]. Spherical particles involving organometal compounds can be used as a building block of nanowires and nano-devices [6–9], and a photochemical method to produce the spherical particles from gaseous mixtures was proposed previously [10]. To produce the spherical aerosol particles more efficiently from a gaseous mixture of $Fe(CO)_5$ and ATMeSi, addition of CS_2 molecules to the gaseous mixture is preferable. In the present study, a ternary gaseous mixture of $Fe(CO)_5$, ATMeSi, and CS_2 was prepared, and the sedimentary aerosol particles were produced under UV light irradiation. Chemical structure of the particles was studied from FT-IR and SEM-EDS analyses. The chemical structure of the sedimentary particles was modified by post-exposure with UV light upon deposited particles. The sedimentary aerosol particles were also produced under a magnetic field and the magnetic field effect on the particle size was studied. Under a regulated convectional flow, the gaseous mixture could produce linearly aggregated particles (i.e., particle wires). Participation of ATMeSi and CS_2 molecules to the production of particle wires was discussed briefly.

2. Experimental

ATMeSi (Tokyo Kasei, G. R. grade), $Fe(CO)_5$ (Kanto, 95%), and CS_2 (Kanto, >99%, G. R. grade) were degassed by freeze-pump-thaw cycles in the dark and purified by vacuum distillation immediately

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* Corresponding author. Tel.: +81 50 1332 5434; fax: +81 43 432 1168.
E-mail address: hmorita@faculty.chiba-u.jp (H. Morita).

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before use. To prepare a gaseous mixture, each vapor was introduced successively into a cross-shaped Pyrex cell (volume 163 cm^3) having a long (length 155 mm, inner diameter 35 mm) and short (length 80 mm, inner diameter 20 mm) arms or into a small cylindrical Pyrex cell (length 160 mm, inner diameter 20 mm, volume 50 cm^3) 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 6×10^{-5} Torr (1 Torr = 133.3 Pa). The partial pressures of $Fe(CO)_5$, ATMeSi, and CS_2 in the irradiation cell were determined from the diagnostic band intensities of FT-IR spectra at 645 cm^{-1} for $Fe(CO)_5$, 1259 cm^{-1} for ATMeSi, and 1531 cm^{-1} for CS_2. The gaseous samples were irradiated with a medium pressure mercury lamp (Ushio UM-452, 450W) through UV29 and UV-D33S filters (energy, 8.8 mJ/s cm^2) to excite both $Fe(CO)_5$ and CS_2 molecules at 313 nm. Absorbance of 1 Torr of $Fe(CO)_5$ and of CS_2 is 0.28 and 0.07, respectively, at 313 nm in 10 cm light path length. Monitor (He-Ne laser) light intensity scattered by the aerosol particles as formed in the irradiation cell during UV light irradiation was measured with a combination of a photomultiplier tube (Hamamatsu 1P28) and a lock-in amplifier (SRS SR-530) through a Y-52 filter. Both the sedimentary particles and the film were deposited on a glass plate and/or Cu substrate placed at the bottom of the irradiation cell.

Scanning electron microscope (SEM) images were recorded with a JEOL JSM 6060 scanning electron microscope, and SEM-EDS analyses were performed using a Philips XL30 CP EDAX scanning electron microscope. FT-IR spectra of the deposits embedded in KBr pellets were measured with a Nicolet NEXUS 470 FT-IR spectrometer. Raman spectra of the sedimentary particles were measured with a Bio Tools chiral Raman RL-1 spectrometer. Magnetic field was applied by a helium-free superconducting magnet (Toshiba TM-5SP).

3. Results and discussion

3.1. Chemical structure of deposits produced from a $Fe(CO)_5$/ATMeSi/CS_2 gaseous mixture

Under UV light irradiation with a medium pressure mercury lamp at 313 for 30 min, a gaseous mixture of $Fe(CO)_5$ (1.7 Torr), ATMeSi (15.9 Torr), and CS_2 (8.9 Torr) produced spherical sedimentary particles of yellowish brown color with a mean diameter of 0.56 μm over the whole glass plate placed at the bottom of the irradiation cell (yield 0.8 mg). SEM image of the deposits on the glass plate is shown in Fig. 1. Besides on the glass plate, solid product was deposited over the cylindrical cell wall during the convection of the gaseous sample (yield 2.3 mg). The amount of the solid product deposited on the cylindrical cell wall was more than the one deposited on the glass plate at the bottom.

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. 2. As was reported previously [2], $Fe(CO)_5$ vapor produced $Fe_2(CO)_9$ with a minor production of $Fe_3(CO)_{12}$ under UV light irradiation. The nucleation and propagation reactions of pure $Fe(CO)_5$ vapor (1.0 Torr) were fast, and the scattered light was detected only for the first 1 min (Fig. 2a). In binary gaseous mixtures of $Fe(CO)_5$ (1.1 Torr) and CS_2 (2.0 Torr) and of $Fe(CO)_5$ (4.7 Torr) and ATMeSi (18 Torr), scattered light was detected for the first 10 and 3 min, respectively (Fig. 2b and c) [2,5]. Incorporation of CS_2 and ATMeSi molecules decelerated the formation of $Fe_2(CO)_9$. In a ternary gaseous mixture of $Fe(CO)_5$ (0.8 Torr), ATMeSi (13.7 Torr), and CS_2 (1.1 Torr), scattered light was detected for the first 10 min (Fig. 2d). As in the binary gaseous mixture, CS_2 and ATMeSi were incorporated into the particle formation process, and chemical species involving these molecules were formed efficiently.

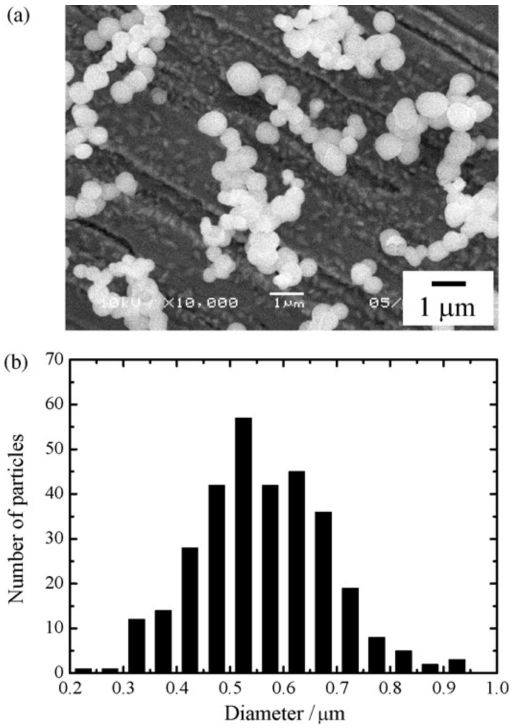

Fig. 1. (a) SEM image of sedimentary aerosol particles produced from a gaseous mixture of $Fe(CO)_5$ (1.7 Torr), ATMeSi (15.9 Torr), and CS_2 (8.9 Torr) under light irradiation with a medium pressure mercury lamp for 30 min and (b) particle size distribution therefrom. Original magnification of SEM, 10,000×.

Chemical processes in the gas phase were investigated by measuring FT-IR spectrum of a gaseous mixture of $Fe(CO)_5$ (1.7 Torr), ATMeSi (15.9 Torr), and CS_2 (8.9 Torr). The spectra before and after light irradiation for 12 min are shown in Fig. 3A. Upon UV light exposure, the FT-IR bands ascribed to $Fe(CO)_5$ significantly decreased their intensities. After allowing for complete sedimentation of the formed aerosol particles, the band intensity (absorbance, A) of $\nu(C{\equiv}O)$ band at 2039 cm^{-1} of $Fe(CO)_5$ [11,12], of $\delta(CH_3)$ band at 1259 cm^{-1} of ATMeSi [13,14], and of $\nu(C{=}S)$ band at 1538 cm^{-1} of CS_2 [15–17] was measured, and the ratio of A to the initial absorbance before light irradiation, A_0, was plotted against cumulative irradiation time (Fig. 3B). In pure vapor, $Fe(CO)_5$ molecules were almost completely consumed in 10 min [2], whereas in the gaseous mixture, they still remained by ~7% even after 30 min. On the other hand, ATMeSi and CS_2 molecules were consumed by only ~5 and ~14%, respectively, during 30 min under light irradiation. Assuming the pseudo first order decay, the depletion rate of $Fe(CO)_5$ molecules was estimated to be $2.3 \times 10^{-3}\ s^{-1}$ for the gaseous mixture and $7.5 \times 10^{-3}\ s^{-1}$ for pure vapor. Depletion of $Fe(CO)_5$ molecules was decelerated by ≈3 times due to the presence of both the ATMeSi and CS_2 molecules. For a binary gaseous mixture of $Fe(CO)_5$ (1.1 Torr) and CS_2 (2.0 Torr), the depletion rate of $Fe(CO)_5$ molecules was $3.5 \times 10^{-3}\ s^{-1}$ [2]. Deceleration of the depletion rate of $Fe(CO)_5$ molecules due to the presence of CS_2 was more efficient than that due to the presence of ATMeSi, indicating that chemical interaction of CS_2 toward $Fe(CO)_5$ was more efficient than that of ATMeSi, and both the CS_2 and ATMeSi molecules prevented $Fe(CO)_5$ molecules from forming $Fe_2(CO)_9$ species.

The number of molecules depleted from the gaseous phase was estimated. In the ternary gaseous mixture of $Fe(CO)_5$ (1.7 Torr),

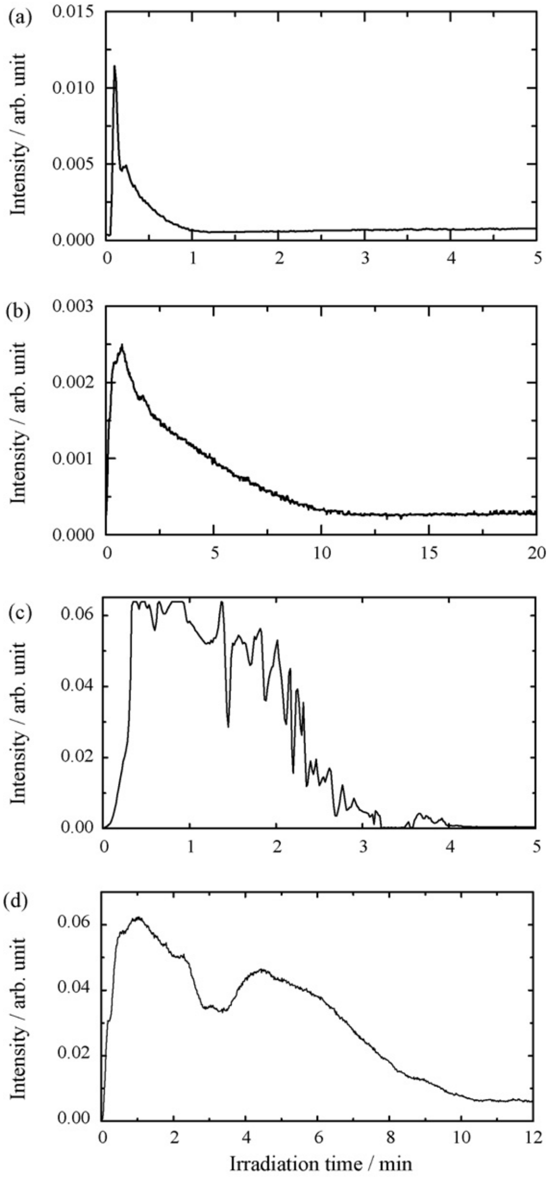

Fig. 2. He-Ne laser light intensity scattered by aerosol particles produced from (a) pure $Fe(CO)_5$ vapor (1.0 Torr), (b) a gaseous mixture of $Fe(CO)_5$ (1.1 Torr) and CS_2 (2.0 Torr), (c) a gaseous mixture of $Fe(CO)_5$ (4.7 Torr) and ATMeSi (18 Torr), and (d) a gaseous mixture of $Fe(CO)_5$ (0.8 Torr), ATMeSi (13.7 Torr), and CS_2 (1.1 Torr) under light irradiation with a medium pressure mercury lamp.

ATMeSi (15.9 Torr), and CS_2 (8.9 Torr), these molecules were depleted by 1.2, 0.7, and 0.6 Torr, respectively, over 10 min under UV light irradiation. For a gaseous mixture containing less amount of CS_2 (i.e., for a gaseous mixture of $Fe(CO)_5$ (0.8 Torr), ATMeSi (13.7 Torr), and CS_2 (1.1 Torr)), the depleted amounts of respective molecules were 0.64, 0.14, and 0.44 Torr over 10 min under UV light irradiation. The number of depleted $Fe(CO)_5$ molecules was almost equal to the sum of the numbers of depleted CS_2 and ATMeSi molecules. In the latter case, the gaseous mixture produced sedimentary aerosol particles during the first 10 min, but it produced a thin film overlaying the sedimentary particles as the final product under a prolonged light irradiation (for 30 min) (Fig. 4). This is due to the fact that CS_2 and $Fe(CO)_5$ molecules were consumed significantly during the first 10 min, and the residual partial pressure of CS_2 (~0.6 Torr) was not high enough to form aerosol particles. Following a chemical tendency of ATMeSi which was the major component of the residual gaseous mixture [5], a thin film

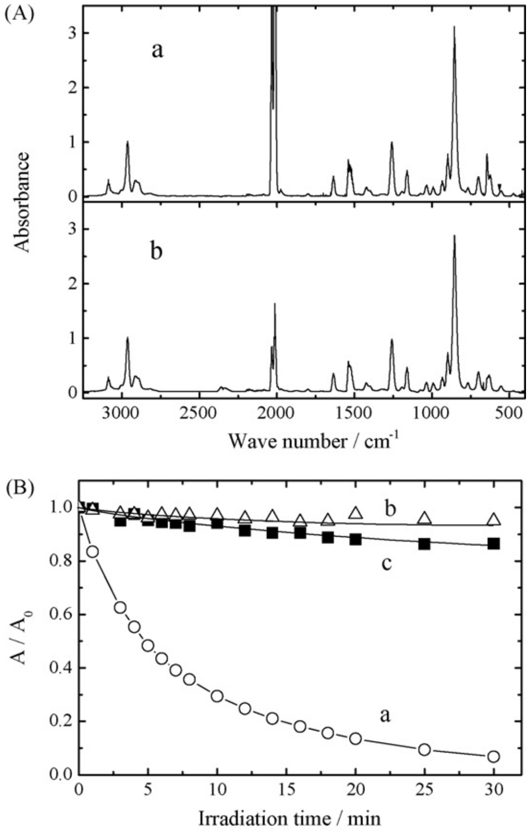

Fig. 3. (A) FT-IR spectra of a gaseous mixture of $Fe(CO)_5$ (1.7 Torr), ATMeSi (15.9 Torr), and CS_2 (8.9 Torr) (a) before and (b) after light irradiation for 12 min. (B) Depletion (A/A_0) of (a) ν(C≡O) band at 2039 cm^{-1} of $Fe(CO)_5$, (b) $\delta(CH_3)$ band at 1259 cm^{-1} of ATMeSi, and (c) ν(C=S) band at 1538 cm^{-1} of CS_2 against irradiation time.

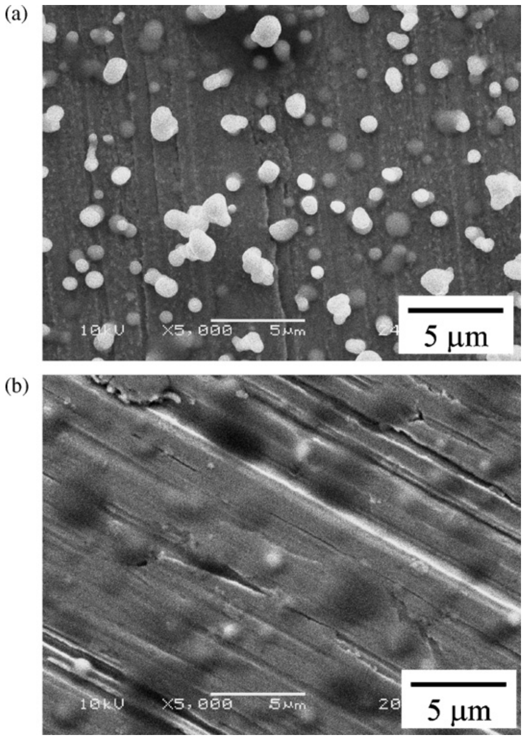

Fig. 4. SEM images of deposits produced from a gaseous mixture of $Fe(CO)_5$ (0.8 Torr), ATMeSi (13.7 Torr), and CS_2 (1.1 Torr) under light irradiation with a medium pressure mercury lamp for (a) 12 min and (b) 30 min. Original magnification of SEM, 5000×.

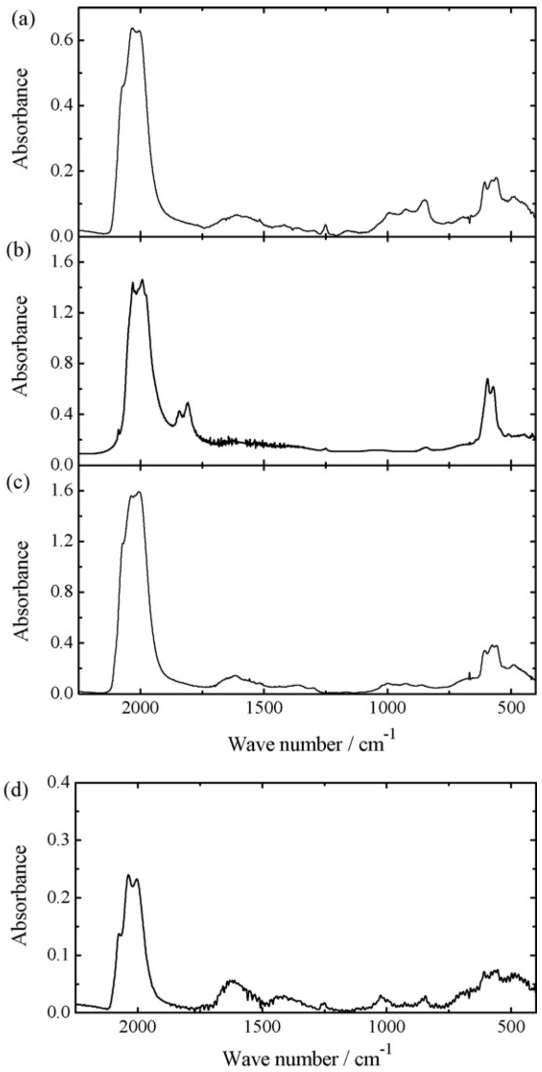

Fig. 5. FT-IR spectra of sedimentary aerosol particles produced from a gaseous mixture of (a) $Fe(CO)_5$ (1.7 Torr), ATMeSi (15.9 Torr), and CS_2 (8.9 Torr), (b) $Fe(CO)_5$ (4.7 Torr) and ATMeSi (18 Torr), and (c) $Fe(CO)_5$ (1.1 Torr) and CS_2 (2.0 Torr) under light irradiation for (a) 12 min, (b) 3 min, and (c) 30 min. (d) FT-IR spectrum after post-exposure for 2 h of deposited particles produced as in the spectrum (a).

was produced after ~15 min under UV light irradiation. To support for this, a gaseous mixture containing more CS_2 molecules (i.e., of $Fe(CO)_5$ (1.3 Torr), ATMeSi (14.7 Torr), and CS_2 (2.6 Torr)) produced only sedimentary aerosol particles during 30 min under light irradiation.

To investigate the chemical structure of the sedimentary particles, FT-IR and Raman spectra and SEM-EDS were measured. FT-IR spectrum of the deposits produced from a gaseous mixture of $Fe(CO)_5$ (1.7 Torr), ATMeSi (15.9 Torr), and CS_2 (8.9 Torr) are shown in Fig. 5a, compared with the spectra of deposits produced from a gaseous mixture of $Fe(CO)_5$ and ATMeSi (Fig. 5b), and of $Fe(CO)_5$ and CS_2 (Fig. 5c). The spectrum showed strong bands in the 2000 cm^{-1} region assigned to ν(C≡O) of the terminal C≡O group, but did not exhibit any bands ascribed to bridging $>$C=O group in the 1800 cm^{-1} region as in the case of the deposits from the binary gaseous mixture of $Fe(CO)_5$ and CS_2 [2]. Weak bands were observed at 1251 and 855 cm^{-1} ascribed to trimethylsilyl group of ATMeSi and at 1612 cm^{-1} originating from CS_2.

SEM-EDS analysis also confirmed the incorporation of ATMeSi and CS_2 molecules into the sedimentary particles. The population of Fe, S, Si, C, and O atoms in the sedimentary particles produced

Table 1
Atomic abundance of Fe, S, and Si atoms in sedimentary aerosol particles produced from a gaseous mixture of $Fe(CO)_5$ (1.7 Torr), ATMeSi (15.9 Torr), and CS_2 (8.9 Torr) as deposited and with post-exposure with a medium pressure mercury lamp for 3 h.

Atomic line	As deposited			With post-exposure		
	At %	Ratio		At %	Ratio	
Fe K	10.0	1	2.5	7.6	1	1.7
S K	4.0	0.40	1	4.5	0.59	1
Si K	0.6	0.06	0.2	0.8	0.11	0.2
C K	51.9	5.2	13.2	53.5	7.2	12.1
O K	33.6	3.4	8.6	33.7	4.5	7.6

from a gaseous mixture of $Fe(CO)_5$ (1.7 Torr), ATMeSi (15.9 Torr), and CS_2 (8.9 Torr) is tabulated in Table 1. The atomic ratio of Fe atom to S and Si atoms was 1:0.40:0.06, showing that CS_2 and ATMeSi molecules were actually incorporated into the formation process of the sedimentary particles. Raman spectrum of the sedimentary aerosol particles produced from a gaseous mixture of $Fe(CO)_5$ (1.7 Torr), ATMeSi (15.9 Torr), and CS_2 (8.9 Torr) is shown in Fig. 6. The spectrum showed a medium band at 155 cm^{-1} assignable to ν(Fe–Fe) and a strong band at 192 cm^{-1} assignable to δ(Fe–S) or δ(C–Fe–C).

During the nucleation process, CS_2 molecules reacted with $Fe(CO)_5$ to decelerate the formation of $Fe_2(CO)_9$. Considering that the bridging CO bond observed in $Fe_2(CO)_9$ almost completely disappeared in the sedimentary particles and δ(Fe–S) band was observed in the Raman spectrum, CS_2 molecules reacted with $Fe(CO)_5$ to connect two Fe atoms. For iron carbonyls, π-coordination of CS_2 molecules and σ-coordination through a sulfur atom were reported in the liquid phase [1,18,19]. Although the present experiment was done in the gaseous phase, $Fe(CO)_4$ species produced from excited $Fe(CO)_5$ may react with CS_2 through either π- or σ-coordination.

$$Fe(CO)_5 + h\nu \rightarrow Fe(CO)_4 + CO \qquad (1)$$

$$Fe(CO)_4 + CS_2 \rightarrow (Fe(CO)_4{\cdot}CS_2) \qquad (2)$$

σ-Coordinated CS_2 can ligate another Fe atom to connect two Fe atoms as was observed for $Co_2(CN)_{10}CS_2$ [1,18].

$$(Fe(CO)_4{\cdot}CS_2) + Fe(CO)_5 \rightarrow Fe(CO)_4\text{–S–C(=S)–}Fe(CO)_4 + CO \qquad (3)$$

For the above complex, ν(C=S) and ν(C–S) bands were expected to appear at 840–980 cm^{-1} region [18].

Thiocarbonyl group can coordinate to Fe atom and combine two transition metal atoms via bridging carbon atom [20–22]. Considering that CS_2 molecules were polymerized in the gas phase mainly

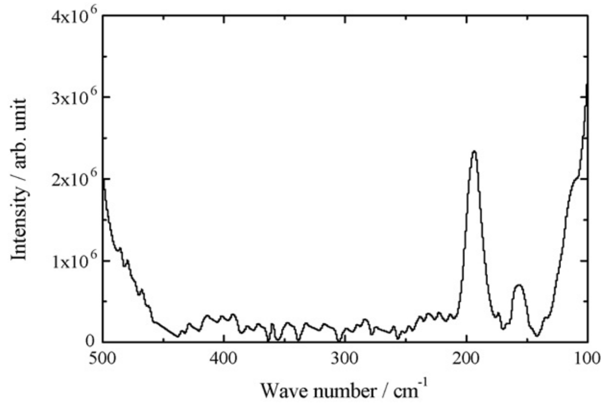

Fig. 6. Raman spectrum of sedimentary aerosol particles produced from a gaseous mixture of $Fe(CO)_5$ (1.7 Torr), ATMeSi (15.9 Torr), and CS_2 (8.9 Torr) under light irradiation for 12 min.

as $(C–S)_n$ under UV light irradiation [23], $Fe(CO)_4$ may react with CS to bridge two Fe atoms through a thiocarbonyl group.

$$CS_2 + h\nu \rightarrow CS_{2*} \quad (4)$$

$$CS_{2*} + CS_2 \rightarrow 2CS + S_2 \quad (5)$$

$$Fe(CO)_4 + CS + Fe(CO)_5 \rightarrow Fe(CO)_4–C(=S)–Fe(CO)_4 + CO \quad (6)$$

Fe–Fe bond may be formed between two Fe atoms connected via carbon-bridging thiocarbonyls as in the case of $[(cyclopentadienyl)Mn(CS)(NO)]_2$ [22]. The observation of ν(Fe–Fe) band in Raman spectrum strongly suggested that chemical structures originating from the species involving σ-coordinated CS_2 (reaction (3)) and from the species involving carbon-bridging thiocarbonyl (reaction (6)) were both formed during aerosol particle formation. As to ATMeSi, FT-IR spectrum of the sedimentary particles showed the bands characteristic of the trimethylsilyl group at 1251 and 855 cm^{-1}. This strongly suggested that ATMeSi ligated to Fe atom via π-coordination of allyl group [24].

$$Fe(CO)_4 + CH_2{=}CH–CH_2–Si(CH_3)_3$$
$$\rightarrow (Fe(CO)_3 \cdot CH_2{=}CH–CH_2–Si(CH_3)_3) + CO \quad (7)$$

The π-coordinated C=C stretching vibrational band was expected to appear at 1470–1534 cm^{-1} [4,25,26]. In FT-IR spectrum (Fig. 5a), several weak bands were observed in this region. One of them may be ascribed to the π-coordinated C=C stretching band.

3.2. Magnetic field effect on a size of sedimentary particles

Magnetic field influenced the formation process of aerosol particles from some gaseous mixtures involving $Fe(CO)_5$ [2,6,7]. Spherical aerosol particles were produced from a gaseous mixture of $Fe(CO)_5$ (1.3 Torr), ATMeSi (17.9 Torr), and CS_2 (2.9 Torr) under a magnetic field up to 5 T. Due to a smaller inner diameter (20 mm) of the cylindrical irradiation cell used in a superconducting magnet [3], the mean diameter of the sedimentary particles decreased to 0.30 μm from 0.56 μm (produced in a cylindrical cell with an inner diameter of 35 mm) in the absence of a magnetic field. Under a magnetic field of 1, 3, and 5 T, the mean diameter increased from 0.30 to 0.31, 0.33, and 0.35 μm, respectively, showing that the chemical reactions during the particle formation were accelerated by the application of a magnetic field. In a preliminary experiment where the third harmonic (355 nm) of pulsed Nd:YAG laser light was exposed on the gaseous mixture, spherical aerosol particles were also produced. SEM-EDS analysis of the sedimentary particles showed that atomic ratio of Si to Fe atom increased with the application of a magnetic field. This result suggested that the π-coordination of ATMeSi (such as in reaction (7)) was accelerated by the application of a magnetic field. Furthermore, in a binary gaseous mixture of $Fe(CO)_5$ and CS_2, photochemical reactivity of $Fe(CO)_5$ was promoted under a magnetic field and the σ-coordinated $(Fe(CO)_4 \cdot CS_2)$ species favored the chemical reaction with $Fe(CO)_5$ [2]. These results strongly suggested that chemical reactions (3) and (7) in the ternary gaseous mixture were accelerated by the application of a magnetic field.

3.3. Control of chemical composition by post-exposure with UV light

For the particles involving metal carbonyl compounds, chemical structure can be changed by exposing UV light on the deposited particles (i.e., by post-exposure). This was successfully performed on the deposited particles produced from a gaseous mixture of $Fe(CO)_5$ and CS_2 [2,3].

Sedimentary particles were produced from a gaseous mixture of $Fe(CO)_5$ (1.7 Torr), ATMeSi (15.9 Torr), and CS_2 (8.9 Torr) under UV light irradiation for 12 min. After evacuating the residual gaseous molecules, the 313 nm light from a medium pressure mercury lamp was irradiated for 2 h on the deposited particles. FT-IR spectrum after the post-exposure is shown in Fig. 5d. Compared to the spectrum before the post-exposure shown in Fig. 5a, the ≈2000 cm^{-1} (2074, 2029, and 2000 cm^{-1}) bands assigned to ν(C≡O) and the 579 cm^{-1} band assigned to δ(Fe–C–O) decreased their intensities compared to the 1612 and the ≈1000 cm^{-1} (1164, 995, 925, and 872 cm^{-1}) bands originating from CS_2. This showed that the terminal C≡O groups were evolved by the post-exposure, accompanying a slight change in the chemical structure of the particles. SEM-EDS analysis was performed on the particles with the post-exposure for 3 h. The result is tabulated in Table 1. Before the post-exposure, atomic ratios of Fe, C, and O to S atom were 2.5, 13.2, and 8.6, but they reduced to 1.7, 12.1, and 7.6 after the post-exposure. This strongly suggested that upon exposure to 313 nm light, volatile fragments such as $Fe(CO)_n$ (n = 1–3) were produced and evolved in addition to CO species.

3.4. Formation of linearly aggregated fine particles

UV light at 313 nm was irradiated on a gaseous mixture of $Fe(CO)_5$ (1.7 Torr), ATMeSi (15.9 Torr), and CS_2 (8.9 Torr) only for a short time (1–2 min) repeatedly (14 times) with an interval of 7 min. This intermittent light irradiation induced a modulated convectional flow of the entire gaseous sample to result in a deposition of linearly aggregated particles (Fig. 7). In Fig. 7a, linearly aggregated particles grew into the space from the front edge of a substrate placed at the bottom of the irradiation cell. Because the deposited particles maintain the photochemical reactivity even after deposition, the adjacent particles can stick to each other through chemical bonds to form chemically bonded linearly aggregated particles (i.e., particle wires) as shown in Fig. 7b. In Fig. 7c where particle wires were produced from a gaseous mixture of $Fe(CO)_5$ (0.9 Torr), ATMeSi (14.3 Torr), and CS_2 (8.7 Torr), particle wires were curved around the edge of the substrate.

From pure $Fe(CO)_5$ vapor at a low pressure (0.2 Torr), a limited number of linearly aggregated particles as long as 50 μm were produced on the substrate under repeated UV light irradiation for a short time (1–2 min) (Fig. 8). On the other hand, a gaseous mixture of $Fe(CO)_5$ (1.1 Torr) and CS_2 (2.0 Torr) deposited mainly randomly aggregated particles together with only a few particle wires as long as ∼15 μm under repeated UV light irradiation for a short time (1–3 s). By adding ATMeSi to a gaseous mixture, particle wires were more easily formed. From the ternary gaseous mixture, particle wires as long as 80 μm (with a mean diameter of 0.4 μm) were produced efficiently as shown in Fig. 7.

CS_2 is a typical molecule which can produce aerosol particles [27–31]. The addition of CS_2 molecules to a gaseous mixture is expected to produce sedimentary particles more easily and hence to form particle wires more efficiently. To study the effect of chemical tendency of CS_2 to form particle wires, both the sedimentary particles and particle wires were produced under light irradiation for 12 min from gaseous mixtures of $Fe(CO)_5$, ATMeSi, and CS_2 in which the partial pressure of CS_2 was varied significantly while those of $Fe(CO)_5$ and ATMeSi remained almost constant. The results are shown in Fig. 9. With increasing partial pressure of CS_2 from 1.1 to 2.6 and further to 8.9 Torr, the length of particle wires increased from 7 to 17 and further to 500 (the longest, 850) μm. The mean diameter of the particles was 0.43 μm in the last case, and the number of particles constituting a single particle wire exceeded to one thousand. In order to produce long particle wires, the partial pressure of CS_2 was needed to be several (∼5)

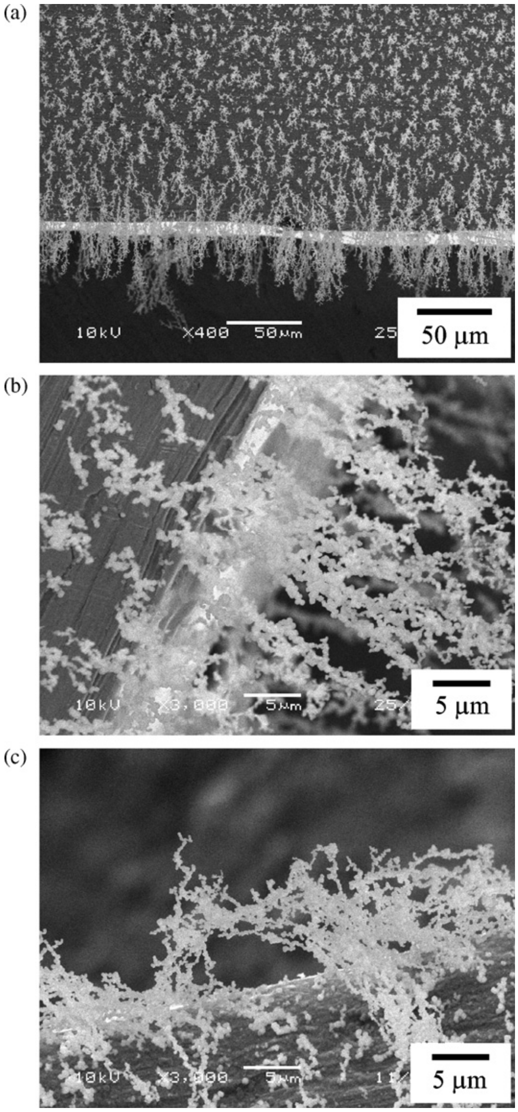

Fig. 7. SEM images of particle wires produced from a gaseous mixture of (a) and (b) $Fe(CO)_5$ (1.7 Torr), ATMeSi (15.9 Torr), and CS_2 (8.9 Torr), and (c) $Fe(CO)_5$ (0.9 Torr), ATMeSi (14.3 Torr), and CS_2 (8.7 Torr) under repeated (14 times) light irradiation for 1–2 min. Original magnification of SEM, (a) 400×, (b) and (c) 3000×.

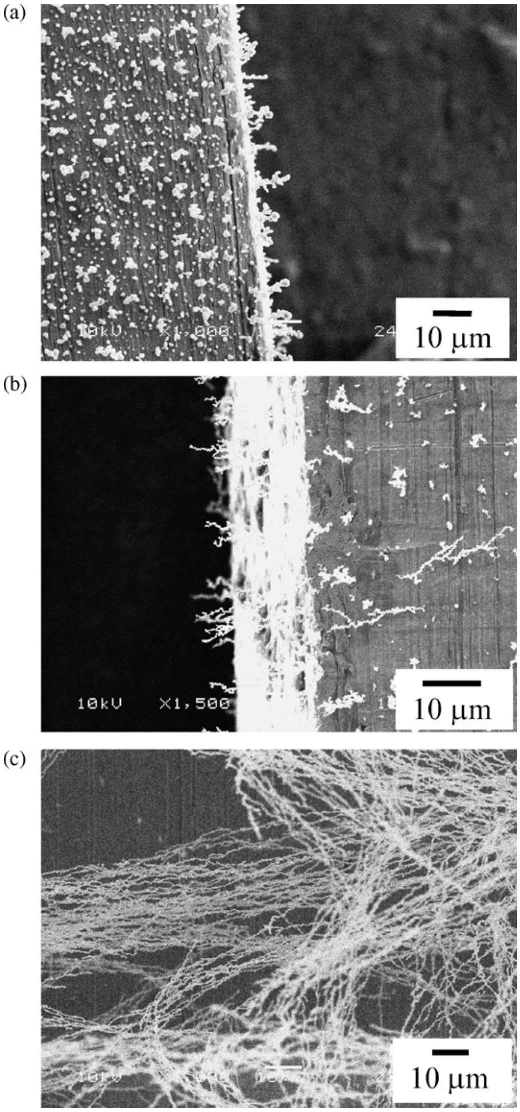

Fig. 9. SEM images of particle wires produced from gaseous mixtures of $Fe(CO)_5$, ATMeSi, and CS_2 with respective partial pressures of (a) 0.8, 13.7, and 1.1 Torr, (b) 1.3, 14.7, and 2.6 Torr, and (c) 1.7, 15.9, and 8.9 Torr under light irradiation for 12 min. Original magnification of SEM, (a) 1000×, (b) 1500×, (c) 1000×.

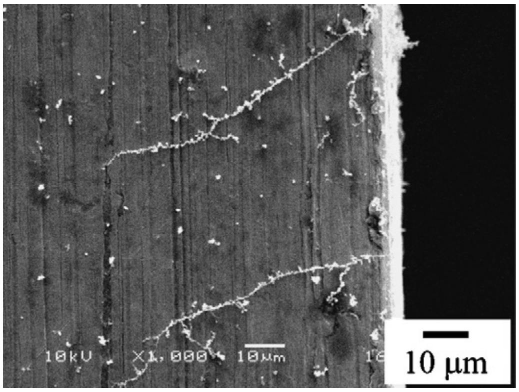

Fig. 8. SEM image of particle wires produced from pure $Fe(CO)_5$ vapor (0.2 Torr) under repeated (7 times) light irradiation for 1–2 min. Original magnification of SEM, 1000×.

times higher than that of $Fe(CO)_5$. A panoramic view of the distribution of particle wires deposited from a gaseous mixture of $Fe(CO)_5$ (1.7 Torr), ATMeSi (15.9 Torr), and CS_2 (8.9 Torr) on a glass plate was shown in Fig. 10. Particle wires as long as several hundreds of μm grew vertically to the surface of a glass plate (placed at the bottom of the irradiation cell) until to 1 mm in depth from the front edge of the glass plate (Fig. 10, spot a). In the deeper region than 1 mm in depth from the front edge, the length of the particle wires became shorter until the region of 5 mm in depth (Fig. 10, spot b). In the region of more than 5 mm in depth, particle wires were no longer formed. Only the aggregated particles were formed (Fig. 10, spot c). As is shown in Fig. 10, both the CS_2 and ATMeSi molecules were effectively incorporated into the particle formation. During the sedimentation process, the long particle wires were produced efficiently in the vicinity of the front edge of the substrate.

The formation of particle wires is characteristic of the sedimentary particles produced by the photochemical method in the gas phase [6]. The particle wire is flexible, and can be connected to another particle wire so as to form a longer wire in any shape.

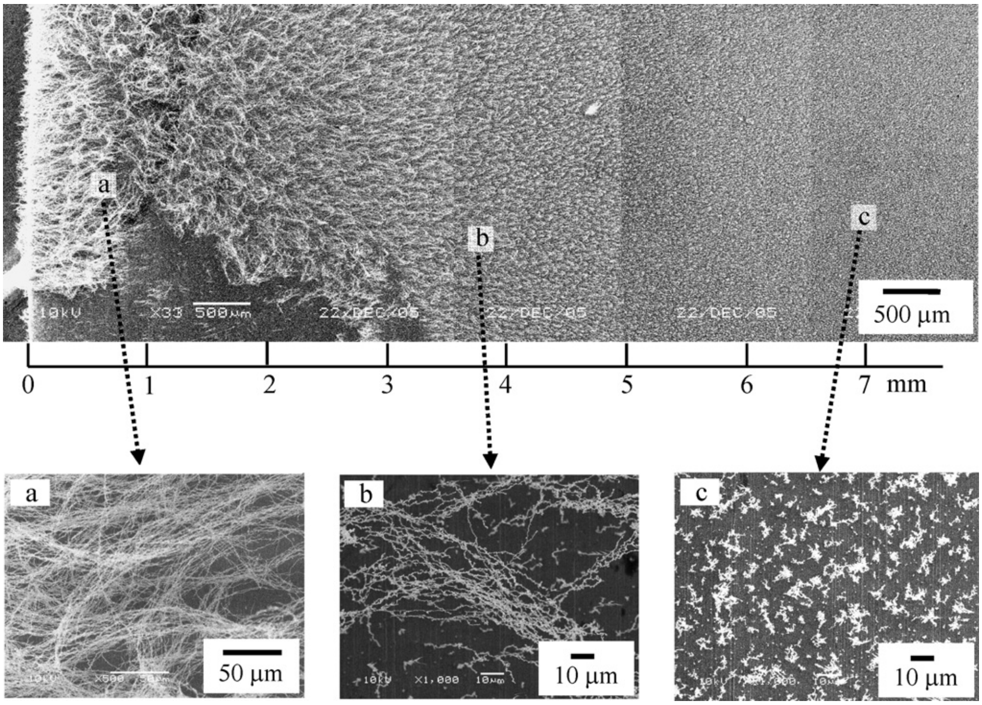

Fig. 10. A panoramic view of the distribution of particle wires deposited from a gaseous mixture of $Fe(CO)_5$ (1.7 Torr), ATMeSi (15.9 Torr), and CS_2 (8.9 Torr) on a glass plate in the region of 0–7 mm in depth. Original magnification of SEM, 33×. Original magnification of SEM at spot (a), 500×, spots (b) and (c), 1000×.

4. Conclusions

From a gaseous mixture of $Fe(CO)_5$, ATMeSi, and CS_2, sedimentary aerosol particles were produced efficiently under UV light irradiation with a medium pressure mercury lamp. From the analysis of chemical structure by FT-IR and Raman spectra, it was strongly suggested that CS_2 reacted with $Fe(CO)_5$ to produce $Fe(CO)_4$–S–C(=S)–$Fe(CO)_4$ species by σ-coordination of CS_2 molecule, that two Fe atoms were bonded via carbon-bridging thiocarbonyls produced from CS_2, and that ATMeSi coordinated to Fe atom via π-coordination of allyl group of ATMeSi. Chemical composition of the deposited particles was changed by the post-exposure with UV light by evolving volatile fragments such as $Fe(CO)_n$ ($n=1$–3) in addition to CO species bonded to Fe atom. During the sedimentation process of the aerosol particles, particle wires were efficiently formed from the gaseous mixture of $Fe(CO)_5$, ATMeSi, and CS_2 at the vicinity of the front edge of a glass plate placed at the bottom of the irradiation cell. When the partial pressure of CS_2 was increased to 5 times higher than that of $Fe(CO)_5$, particle wires as long as 500 μm with a mean diameter of 0.4 μm were formed efficiently.

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