

# Particle size dependence of chemical compositions of metal-containing ultrafine particles synthesized from a gaseous mixture of iron pentacarbonyl and carbon disulfide

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## Abstract

From a gaseous mixture of  $\text{Fe}(\text{CO})_5$  and  $\text{CS}_2$ , sedimentary aerosol particles involving organometal compounds were produced under UV light irradiation at 313 nm. By shortening the irradiation time of UV light, the particle size was effectively diminished to as small as 58 nm. From the analysis of the chemical structure by EDX-SEM and FT-IR spectra, chemical compositions of the particles smaller than 80 nm were found to be different from those of larger particles in that more CO groups were evolved, suggesting that the chemical reactions during the nucleation process were different from those during the propagation process. Chemical reactions during aerosol particle formation were discussed based on the chemical compositions of the sedimentary particles, and formation of sulfur-bridged Fe clusters was suggested during the nucleation process. By post-exposure with 266 nm light upon the deposited particles, volatile fragments such as  $\text{Fe}(\text{CO})_n$  ( $n = 1-3$ ) were evolved in addition to CO. © 2008 Elsevier B.V. All rights reserved.

**Keywords:** Ultrafine particles; Gas phase photochemical reaction; Particle size; Iron pentacarbonyl; Carbon disulfide

## 1. Introduction

Using photochemical reactions of gaseous molecules, ultrafine particles can be produced from some gaseous mixtures involving acrolein [1,2], carbon disulfide ( $\text{CS}_2$ ) [2,3], and organosilicon compounds [4–7]. This method (called hereafter the photochemical method) was applied to some gaseous mixtures involving organometal compounds, and succeeded in producing ultrafine particles which involved organometal complexes [8–10]. In a previous paper [11], from a gaseous mixture of iron pentacarbonyl ( $\text{Fe}(\text{CO})_5$ ) and  $\text{CS}_2$ , ultrafine particles were produced, and the change of chemical structure of the particles was investigated by applying a magnetic field during photochemical reactions [12–15] or alternatively

by irradiating UV light upon the sedimentary particles already deposited on a substrate in order to initiate solid-state photochemical reactions in the particles (post-exposure with UV light) [16].

Ultrafine particles can be used as building blocks of nano-wires and nano-devices. For this particular use, it is preferable to synthesize spherical particles having the same diameter. In the photochemical method, the particle size may change by varying exciting light intensity, light irradiation time, and ambient temperature, which regulate the reaction rate and the reaction time of the nucleation and the propagation processes. In the present study, taking these into account, aerosol particles were produced from a gaseous mixture of  $\text{Fe}(\text{CO})_5$  and  $\text{CS}_2$  under various experimental conditions; the particle size distribution of the sedimentary particles was measured from SEM images, and the chemical structure of the particles was studied from the analysis of EDX-SEM and FT-IR spectra. From these results, irradiation time dependence of the particle size and of the chemical structure was studied, and chemical reactions during the nucleation

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process were discussed compared to those during the propagation process of the particle formation.

## 2. Experimental

Fe(CO)<sub>5</sub> (Kanto, 95%) and CS<sub>2</sub> (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 cm<sup>3</sup>) 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)<sub>5</sub> and CS<sub>2</sub> in the irradiation cell were determined from the diagnostic band intensities of FT-IR spectra at 645 cm<sup>-1</sup> for Fe(CO)<sub>5</sub> and 1530 cm<sup>-1</sup> for CS<sub>2</sub>. The gaseous samples were irradiated with a medium pressure mercury lamp (Ushio UM-452, 450W) through a UV29 and a UVD33S filters (energy, 5.4 mJ/s cm<sup>2</sup>) to excite both Fe(CO)<sub>5</sub> and CS<sub>2</sub> molecules at 313 nm. Absorbance of 1 Torr of Fe(CO)<sub>5</sub> and CS<sub>2</sub> vapors is 0.28 and 0.011, respectively, at 313 nm in 10 cm light path length. Fe(CO)<sub>5</sub> was excited more ( $\approx 25$  times) efficiently than CS<sub>2</sub>. 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 (EMI 6256S) and a lock-in amplifier (SRS SR-530) through a Y-52 filter. The aerosol particles were deposited on a glass plate and/or Cu substrate accommodated in the irradiation cell. Scanning electron microscope (SEM) images were recorded with a JEOL JSM 6060 scanning electron microscope, and EDX-SEM analyses were performed using a Philips XL30 CP scanning electron microscope. The sedimentary aerosol particles were mixed with KBr powder to prepare KBr pellets and FT-IR spectra of the sedimentary particles embedded in the pellets were measured with a Nicolet NEXUS 470 FT-IR spectrometer. In order to change the chemical structure of the deposited particles, the fourth harmonic (266 nm) of a pulsed Nd:YAG laser light (Continuum Surelite I-10, pulse width 6 ns, repetition rate 10 Hz) was irradiated on the deposited particles.

## 3. Results and discussion

### 3.1. Chemical structure of sedimentary particles produced from Fe(CO)<sub>5</sub> and CS<sub>2</sub>

Under UV light irradiation at 313 nm for 10 min, a gaseous mixture of Fe(CO)<sub>5</sub> (1.1 Torr) and CS<sub>2</sub> (1.9 Torr) produced spherical sedimentary aerosol particles with a mean diameter of 0.31  $\mu\text{m}$  as shown in Fig. 1. FT-IR spectrum of the sedimentary aerosol particles (Fig. 2(a)) exhibited the C $\equiv$ O stretching bands at 2005, 2037, and 2080 cm<sup>-1</sup>, but not the C=O stretching band at 1825 cm<sup>-1</sup> which was observed with Fe<sub>2</sub>(CO)<sub>9</sub> [17,18] deposited from pure Fe(CO)<sub>5</sub> vapor (Fig. 2(b)). These results indicated that Fe–C(=O)–Fe chemical bond was not formed by the incorporation of CS<sub>2</sub> molecules. In addition, FT-IR bands observed with the sedimentary aerosol particles produced from

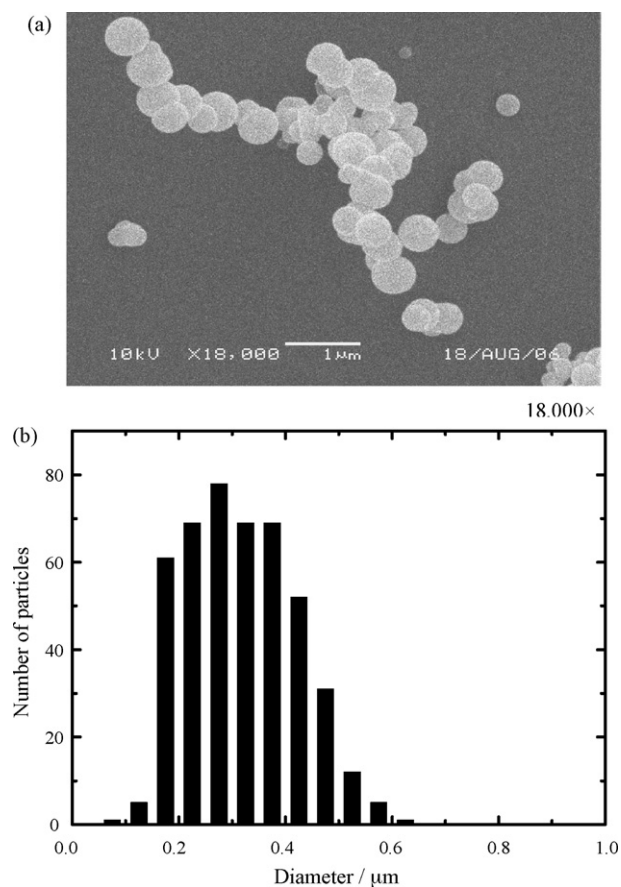


Fig. 1. (a) SEM image of sedimentary particles deposited from a gaseous mixture of Fe(CO)<sub>5</sub> (1.1 Torr) and CS<sub>2</sub> (1.9 Torr) under light irradiation at 313 nm for 10 min, and (b) particle size distribution therefrom. Original magnification of SEM 18,000 $\times$ .

pure CS<sub>2</sub> vapor (Fig. 2(c)) [19–24] almost disappeared, supporting that the bond formation between Fe(CO)<sub>4</sub> (originating from Fe(CO)<sub>5</sub> [25]) and CS<sub>2</sub> molecules was the primary chemical reaction of the gaseous mixture as suggested previously [11].

This was further supported from EDX-SEM analysis. The population of Fe, S, C, and O atoms in the sedimentary particles is tabulated in Table 1. The atomic ratio of Fe atom to S atom was 1:0.15, showing that CS<sub>2</sub> molecules were actually incorporated into the aerosol particles. CS<sub>2</sub> molecules are known to be activated by transition metal complexes in the liquid phase [26,27]. For iron carbonyls,  $\pi$ -coordination of CS<sub>2</sub> molecules and  $\sigma$ -coordination through a sulfur atom are reported [28]. Although the present experiment was done in the gaseous phase, Fe(CO)<sub>4</sub>

Table 1  
Population of atoms in sedimentary particles produced from a gaseous mixture of Fe(CO)<sub>5</sub> (1.1 Torr) and CS<sub>2</sub> (1.9 Torr) before and after post-exposure with pulsed Nd:YAG laser light (266 nm)

| Atomic line | As deposited |       | With post-exposure |       |      |     |
|-------------|--------------|-------|--------------------|-------|------|-----|
|             | At (%)       | Ratio | At (%)             | Ratio |      |     |
| Fe K        | 15.9         | 1     | 6.5                | 21.0  | 1    | 4.2 |
| S K         | 2.4          | 0.15  | 1                  | 5.0   | 0.24 | 1   |
| C K         | 39.0         | 2.45  | 16                 | 38.2  | 1.82 | 7.6 |
| O K         | 42.7         | 2.69  | 17                 | 35.8  | 1.71 | 7.1 |

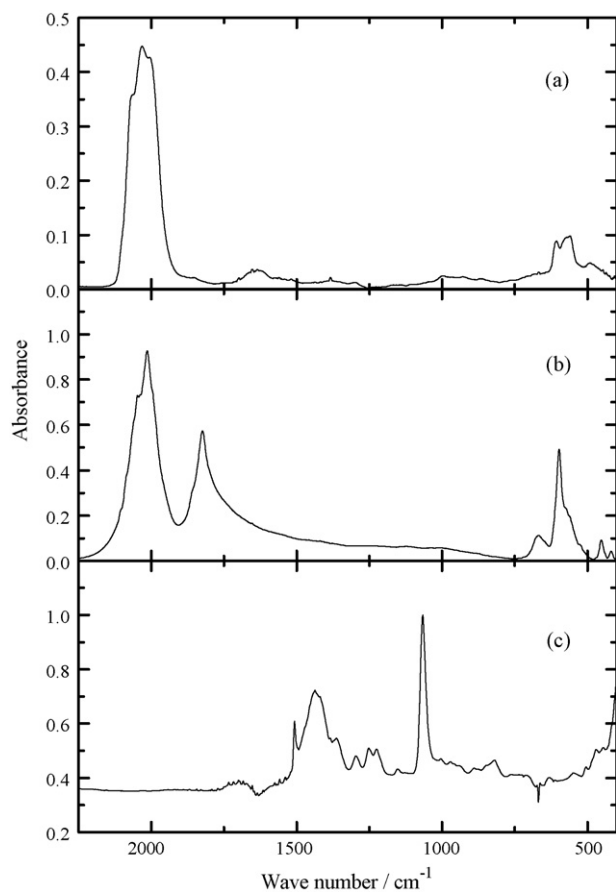
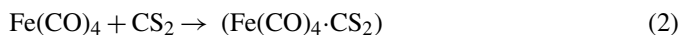
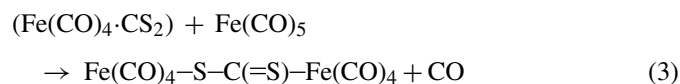


Fig. 2. FT-IR spectra of deposits produced from (a) a gaseous mixture of  $\text{Fe}(\text{CO})_5$  (1.1 Torr) and  $\text{CS}_2$  (1.9 Torr), (b) pure  $\text{Fe}(\text{CO})_5$  vapor (1.0 Torr), and (c) pure  $\text{CS}_2$  vapor (50 Torr) under light irradiation at 313 nm for (a) 10 min, (b) 10 min, and (c) 2 h.

species produced from excited  $\text{Fe}(\text{CO})_5$  may react with  $\text{CS}_2$  molecules through either  $\pi$ - or  $\sigma$ -coordination.

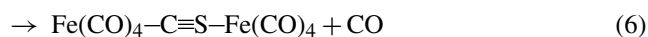
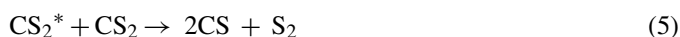


$\sigma$ -Coordinated  $\text{CS}_2$  can ligate another Fe atom to connect two Fe atoms as was observed for  $\text{Co}_2(\text{CN})_{10}\text{CS}_2$  [26,27].



For the above complex,  $\nu(\text{C}=\text{S})$  and  $\nu(\text{C—S})$  bands were expected to appear at  $840\text{--}980\text{ cm}^{-1}$  region [26].

Thiocarbonyl group can add to  $\text{Fe}(\text{CO})_4$  to form  $\text{Fe}(\text{CO})_4(\text{CS})$  [29–31], and combine two transition metal atoms by end-to-end bridging of a thiocarbonyl,  $M\text{—C}\equiv\text{S—M}$  [32]. Considering that  $\text{CS}_2$  molecules were polymerized in the gas phase mainly as  $(\text{C—S})_n$  under UV light irradiation [19], photo-excited  $\text{Fe}(\text{CO})_5$  may react with  $\text{CS}_2$  to bridge two iron atoms through a thiocarbonyl group.



FT-IR band of an end-to-end bridging thiocarbonyl was not identified as yet, although it was expected to appear near  $1100\text{ cm}^{-1}$  [32]. Judging from FT-IR spectrum of the sedimentary particles in Fig. 2 where several bands were observed in  $900\text{--}1100\text{ cm}^{-1}$  region, two Fe atoms may possibly be connected either by  $\sigma$ -coordinated  $\text{CS}_2$  (reaction (3)) and/or by end-to-end bridging of a thiocarbonyl (reaction (6)).

From the depletion of FT-IR band intensities of the gaseous molecules, the molar ratio of depleted  $\text{Fe}(\text{CO})_5$  and  $\text{CS}_2$  molecules in the gas phase was estimated to be 5:1 in the previous paper [11]. This value is close to the atomic ratio of Fe atom to S atom analyzed by EDX-SEM, supporting for the bridging by a thiocarbonyl group originating from  $\text{CS}_2$  (reaction (6)). In the EDX-SEM analysis, the signal of the Cu substrate was detected. This indicates that some fraction of the O and also of the C signals can originate from the surface contamination and oxidation of uncovered area of the substrate present prior to the particle deposition. Taking this into account, atomic ratios of the C and O atoms to Fe atom are maximum values. In Table 1, the atomic ratio of Fe to C was 1:2.5, and that of Fe to O was 1:2.7. These values strongly suggested that iron carbonyls were present as  $\text{Fe}(\text{CO})_3$  and/or  $\text{Fe}(\text{CO})_2$  groups in the sedimentary particles. A chemical structure with sulfur bridged triangular Fe atoms was reported in  $\text{HFe}_3(\text{CO})_8\text{NOS}$  cluster [33]. This chemical structure does not have any bridging  $\text{C}=\text{O}$  group. Considering a variety of possible structures of metal carbonyl complexes containing S atoms, the sedimentary aerosol particles are believed to be composed of several chemical species, and the chemical species with sulfur bridged Fe atoms is one of the plausible chemical structure of the particles.

### 3.2. Post exposure with YAG laser light on deposited particles

Chemical structure of the sedimentary particles can be changed by irradiating UV light on the deposited particles (i.e., by post-exposure) as was successfully done in the previous paper [11]. In the present paper, instead of using 313 nm light from a medium pressure mercury lamp [11], the fourth harmonic (266 nm) of pulsed Nd:YAG laser light was irradiated on the sedimentary particles which were produced from a gaseous mixture of  $\text{Fe}(\text{CO})_5$  (1.1 Torr) and  $\text{CS}_2$  (1.9 Torr) under light irradiation at 313 nm for 10 min. Under direct irradiation of YAG laser light ( $100\text{ mJ/pulse cm}^2$ ), the particles with a mean diameter of 310 nm were decomposed into smaller particles with a mean diameter of 30 nm. With decreasing laser power to  $32\text{ mJ/pulse cm}^2$ , the particles tended to fuse to form bigger deposits. In order to avoid the effect of intense laser light mentioned above, the laser light was defocused using a concave lens to reduce the energy ( $5\text{ mJ/pulse cm}^2$ ) and was irradiated on the particles. FT-IR spectra of the particles before and after the post-exposure for 1 h are shown in Fig. 3(a) and (b). In Fig. 3(b), the  $\approx 2000\text{ cm}^{-1}$  (2080, 2037, and  $2005\text{ cm}^{-1}$ ) bands assigned to

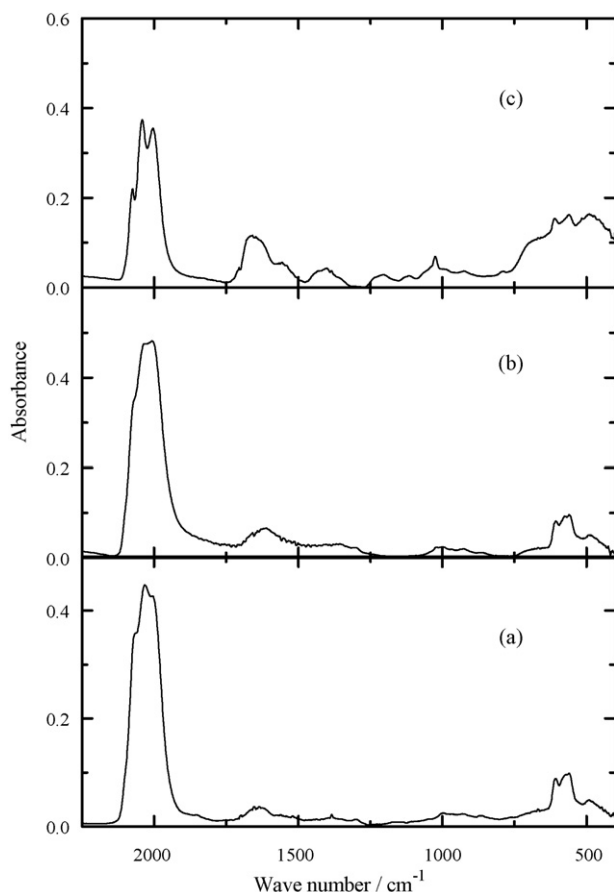


Fig. 3. FT-IR spectra of sedimentary particles deposited from a gaseous mixture of  $\text{Fe}(\text{CO})_5$  (1.1 Torr) and  $\text{CS}_2$  (1.9 Torr) under light irradiation at 313 nm for 10 min (a) before and (b) after post-exposure with pulsed Nd:YAG laser light (266 nm) for 1 h, and (c) after post-exposure with a mercury lamp (313 nm) for 2 h.

$\nu(\text{C}\equiv\text{O})$  and 607 and 576  $\text{cm}^{-1}$  bands assigned to  $\delta(\text{Fe}-\text{C}-\text{O})$  decreased their intensities compared to the intensities of  $\approx 1650$  and  $\approx 1000$   $\text{cm}^{-1}$  bands originating from  $\text{CS}_2$ . This showed that terminal  $\text{C}\equiv\text{O}$  groups were evolved by the post-exposure with pulsed Nd:YAG laser light. For the purpose of comparison, the spectrum after the post-exposure with a mercury lamp for 2 h reported previously [11] is shown in Fig. 3(c). By the post-exposure with a mercury lamp for long time, evolving of  $\text{C}\equiv\text{O}$  groups was seen more clearly. Population of atoms in the particles after the post-exposure with a pulsed Nd:YAG laser was analyzed by EDX-SEM. The result is tabulated in Table 1. Before the post-exposure, atomic ratio of C (and O) to Fe atom was roughly 2.5:1, but it reduced to 1.7:1 after the post-exposure, indicating that CO groups were evolved by the post-exposure. Furthermore, atomic ratio of Fe to S reduced to 4.2:1 after the post-exposure. This strongly suggested that upon irradiation with 266 nm light, volatile fragments such as  $\text{Fe}(\text{CO})_n$  ( $n = 1-3$ ) were produced and evolved in addition to CO species.

### 3.3. Control of particle size

In the synthesis of ultrafine particles in the gas phase, light irradiation induces the convection of entire gaseous sample. The aerosol particles produced under light irradiation travel along the

cylindrical cell wall due to convection. During the entire period of travelling, aerosol particles continue to grow by colliding with excited molecules (gas-to-particle conversion) during nucleation mode and then by colliding with other particles (coagulation) during accumulation mode, and finally collide with the substrate accommodated at the bottom of the irradiation cell within one cycle of the convection. Hence, the particle size is expected to change by varying the exciting light intensity, light irradiation time, and ambient temperature which regulate the reaction rate and the reaction time. In order to evaluate the effect of these experimental parameters on the particle size, aerosol particles were produced from a gaseous mixture of  $\text{Fe}(\text{CO})_5$  (1.4 Torr) and  $\text{CS}_2$  (1.6 Torr) under different experimental conditions. In the present experimental set-up, light intensity decreased along the propagation direction of light. Light intensity at the front side of the irradiation cell decreased by 40% at the rear side of the irradiation cell, and the mean diameter of particles deposited at the front side decreased by 20% at the rear side. Based on these experimental results, sedimentary particles deposited at the front side of the irradiation cell were used to determine and compare the mean diameter of the particles produced under various experimental conditions.

At first, in order to reduce the reaction rate during aerosol particle formation, UV light intensity from a mercury lamp was reduced from 5.4 to 1.4  $\text{mJ}/\text{cm}^2$  s at the front side of the irradiation cell. The mean diameter of the sedimentary particles determined from SEM images reduced from 270 to 215 nm using a cylindrical cell with inner diameter of 20 mm. Furthermore, ambient temperature was lowered from 22 to 5 °C. This caused a smaller mean diameter from 215 to 172 nm. These results clearly showed that the particle size of the aerosol particles was actually controlled by changing the chemical reaction rate.

In a cylindrical cell with a larger diameter, the period of convection of entire gaseous sample becomes longer under stationary light irradiation. This causes the longer propagation time during aerosol particle formation. Hence, the inner diameter of a cylindrical cell was increased from 20 to 35 mm. Although the partial pressure of the gaseous mixture changed to  $\text{Fe}(\text{CO})_5$  (1.1 Torr) and  $\text{CS}_2$  (1.9 Torr) in a cell with inner diameter of 35 mm due to the sample preparation procedure, the mean diameter of the sedimentary particles increased from 270 (in a cell with inner diameter of 20 mm) to 310 nm under UV light intensity of 5.4  $\text{mJ}/\text{cm}^2$  s, supporting the longer propagation time of the particle growth was actually fulfilled using the irradiation cell with a larger diameter.

In the nucleation mode during the propagation process, the nucleation starts photochemically and gas-to-particle conversion takes place only when the gaseous molecules are irradiated with UV light. Hence, the propagation time of the nucleation mode can be controlled directly by changing the irradiation time of UV light. For a gaseous mixture of  $\text{Fe}(\text{CO})_5$  (1.1 Torr) and  $\text{CS}_2$  (1.9 Torr), monitor (He-Ne laser) light intensity scattered by the aerosol particles was measured under UV light irradiation only for 2.5 s. The scattered light intensity increased during and shortly after light irradiation until 6 s, and then decreased until the scattered light completely disappeared after 45 s. This result indicated that the convection period of the gaseous sample was

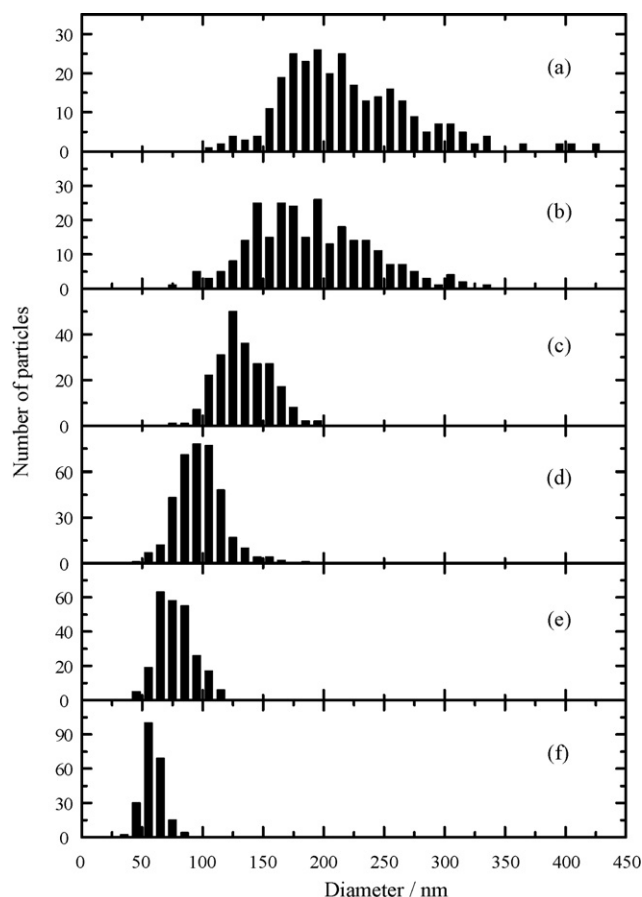


Fig. 4. Particle size distributions of sedimentary particles deposited from a gaseous mixture of  $\text{Fe}(\text{CO})_5$  (1.1 Torr) and  $\text{CS}_2$  (1.9 Torr) under light irradiation at 313 nm for (a) 120, (b) 60, (c) 10, (d) 5, (e) 2.5, and (f) 1 s. The mean diameter is (a) 220, (b) 190, (c) 130, (d) 97, (e) 77, and (f) 58 nm.

about 51 s. In this experiment, taking this into account, UV light irradiation within the same short period was repeated several times with an interval of 60 s. This interval allowed complete sedimentation of the formed aerosol particles onto the substrate. Repeated light irradiation produced sedimentary aerosol particles with a high product yield enough to be able to determine the particle size distribution from SEM images. The fixed irradiation time was shortened from 120 to 1 s, and the particle size distributions were measured; the results are shown in Fig. 4. The mean diameter of the particles was 220, 190, 130, 97, 77, and 58 nm under light irradiation for 120, 60, 10, 5, 2.5, and 1 s, respectively. With shorter irradiation time, the mean diameter of the sedimentary particles became smaller until to 58 nm. In Fig. 5, the mean diameter was plotted as a function of the cube root of the irradiation time. A good linear relationship holds for the particles with mean diameters of less than 100 nm, to which the nucleation mode of particle growth dominates. The linear relationship showed that the number of molecules incorporated into the particles was roughly proportional to the reaction time. These results demonstrated that in the photochemical method, the size of aerosol particles was effectively controlled by changing the irradiation time. Controllability of the particle size by this way is an advantage of the photochemical method.

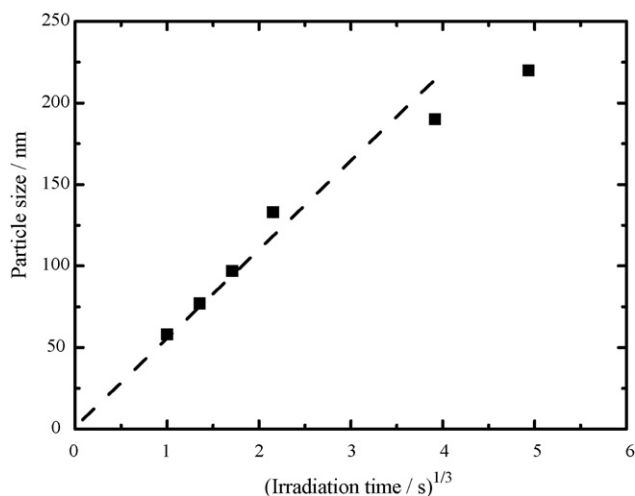


Fig. 5. Mean diameters of the sedimentary particles as a function of the cube root of the irradiation time.

To investigate whether chemical structure of the particles depended on the particle size, FT-IR spectra of the sedimentary particles produced under different light irradiation time were measured, and the results are shown in Fig. 6. Compared to the spectrum of the particles produced under light irradiation for 10 min (Figs. 2(a) and 3(a)), the particles produced under light irradiation for as short as 5 s did not show any significant change in their spectra. For the particles as small as 77 nm

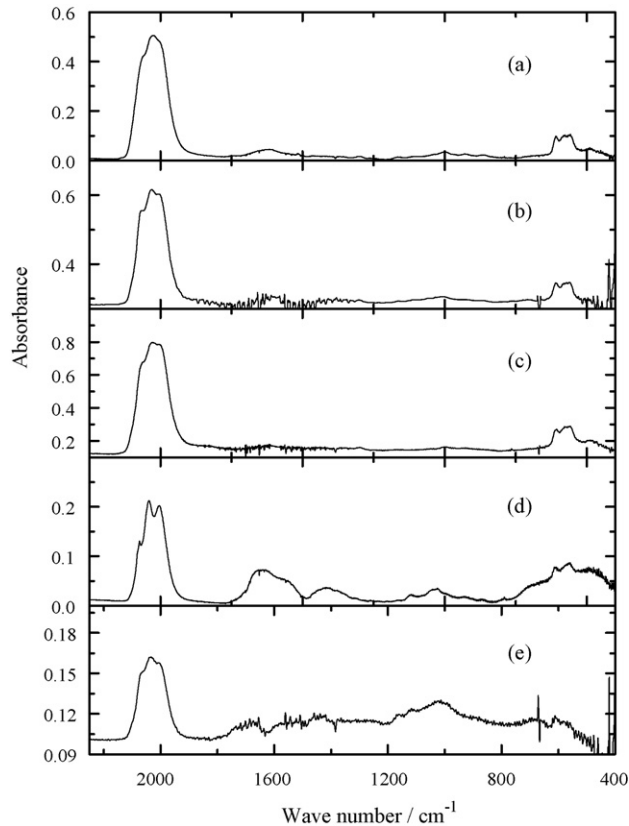


Fig. 6. FT-IR spectra of sedimentary particles deposited from a gaseous mixture of  $\text{Fe}(\text{CO})_5$  (1.1 Torr) and  $\text{CS}_2$  (1.9 Torr) under light irradiation at 313 nm for (a) 120, (b) 60, (c) 5, (d) 2.5, and (e) 1 s.

Table 2

Population of atoms in sedimentary particles produced from a gaseous mixture of Fe(CO)<sub>5</sub> (1.1 Torr) and CS<sub>2</sub> (1.9 Torr) under repeated light irradiation for 1 s

| Atomic line | At (%) | Ratio |     |
|-------------|--------|-------|-----|
| Fe L        | 13.8   | 1     | 6.3 |
| S K         | 2.2    | 0.16  | 1   |
| C K         | 28.7   | 2.08  | 13  |
| O K         | 17.1   | 1.25  | 7.9 |
| Cu L        | 38.3   | 2.78  | 18  |

(irradiation time: 2.5 s) and 58 nm (irradiation time: 1 s), FT-IR bands at  $\approx 2000$ , 607, and 576 cm<sup>-1</sup> decreased their intensities. The particles with a mean diameter of 58 nm were analyzed by EDX-SEM. The result is tabulated in Table 2. In the analysis, due to the small particle size, uncovered area of Cu substrate, hence, the signal of the Cu substrate increased, and atomic percent of Cu reached to 35–45% at four different measuring spots. Considering that some fraction of the O and also of the C signals originated from the surface contamination and oxidation of the substrate, the result was compared to those in Table 1. In the small particles, population of the C and especially of the O atoms decreased considerably, whereas the ratio of Fe to S atom was almost constant regardless of the particle size. This strongly suggested that in the nucleation reaction, Fe(CO)<sub>5</sub> molecules reacted with CS<sub>2</sub> molecules by evolving several (3–4) CO groups and formed a cluster containing less oxygen atom. Sulfur bridged Fe clusters [33] and some chemical species involving (Fe–S)<sub>4</sub> cubane structure [34] may be candidates for the chemical structure in the nucleation process. In the propagation process, chemical reactions (3) and (6) may become favorable.

#### 4. Conclusions

By shortening the irradiation time of UV light, the particle size was effectively diminished to as small as 58 nm for the sedimentary aerosol particles synthesized from a gaseous mixture of Fe(CO)<sub>5</sub> and CS<sub>2</sub>. From the analysis of the chemical structure by EDX-SEM and FT-IR spectra, chemical compositions of the particles smaller than 80 nm were different from those of larger particles in that more CO groups and O atoms were evolved. This strongly suggested that chemical reactions during the nucleation process were different from those during the

propagation process, and formation of sulfur-bridged Fe clusters was suggested to be favored during the nucleation process. By the post-exposure with 266 nm light on the deposited particles, volatile fragments such as Fe(CO)<sub>n</sub> ( $n = 1–3$ ) were evolved in addition to CO species.

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