CHEMISTRY LETTERS, pp. 411-414, 1992.

Infrared Spectrum of Veins-of-Leaf Cluster in Laser-Induced Aerosol Formation from CS_2 Vapor

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A veins-of-leaf cluster is formed on the window surface of a reaction cell in N_2-laser-induced aerosol formation from CS_2 vapor. The infrared spectrum of this cluster is similar to that of the floating substance collected on a small KBr plate placed in the center of the reaction cell, and rather different from that of the sedimentary material. It is noteworthy that there are characteristic bands, which are present only in the spectrum of this cluster. The X-ray diffraction analysis indicates that an amorphous structure is much major in the cluster.

A brown solid sediment was found in the flash-photolysis experiment of CS_2 vapor by Sorgo et al.;[1] thereafter Ernst and Hoffman[2] confirmed that it is also formed by N_2-laser irradiation to CS_2 vapor. Since then, Ernst and Hoffman,[2-4] Wen et al.,[5] and Vlahoyanis et al.[6] have extensively studied the aerosol formation. One of the present authors (AM)[7-10] studied dynamics of the aerosol formation in detail. The constituents of the aerosol have been proposed to be carbon monosulfide polymers, $(CS)_n$,[2] and carbon disulfide polymers, $(CS_2)_n$,[5] without any definite experimental ground. Very recently, our spectroscopic experiments[11,12] showed that the possibility for the existence of these C-S polymers is excluded; that the aerosol is a mixture of carbon polymers, C_n, and sulfur polymers, S_n. Furthermore we found that the sediment consists of uniform-sized spherical aerosol particles and their CCA (cluster-cluster aggregation) aerosol clusters; that DLP (diffusion-limited precipitation) clusters, whose shapes are like the veins of a leaf, are formed on the window surface of the reaction cell. In the present study, the infrared spectrum of the DLP cluster is measured and compared with those of the sediment and the substance floating in the reaction cell. Besides, the crystalline structure in the DLP cluster is surveyed.

The samples were formed by N_2-laser (Lambda Physik EMG102) irradiation to CS_2 vapor introduced at a pressure of 50-100 Torr in a cylindrical pyrex-glass cell (25 mmϕ in diameter, 100 mm in length) with quartz windows. The laser repetition rate was 10 Hz, and the total radiation time was 50 hours. The laser beam was not focused. Reagent-grade carbon disulfide was purified through repeated freeze-pump-thaw cycles under the vacuum, and finally by vacuum distillation. We used a Bruker 113V FTIR spectrometer and a JASCO LA1000 spectrophotometer for infrared and visible-ultraviolet spectroscopy, respectively. More experimental details are described elsewhere.[11,12]

A needle-like material grows on the window surface of the reaction cell in the region irradiated by an N_2-laser beam, as shown in Fig.1. The optical microscope image of this material shows the pattern like the veins of a leaf, as shown in Fig.2. This type of cluster is formed in diffusion-limited precipitation (DLP), when the spatial distribution of molecular species is expressed in terms of Poisson's equation.[13,14] On the other hand, the optical microscope image of the floating substance, which was collected on the small glass plate placed in the center of the reaction cell, indicates that the floating substance rather uniformly adheres to the plate; that no fine ordered pattern like the DLP cluster is found.

The difference between the DLP cluster and the deposit of the floating substance is considered to be due to the spatial inhomogeneity in the concentration of floating adhesion-species; the DLP cluster is formed, when the gradient of the concentration of floating adhesion-species is large near the glass surface. Since the floating adhesion-species populate densely and homogeneously in the center of the reaction cell, the gradient will be very

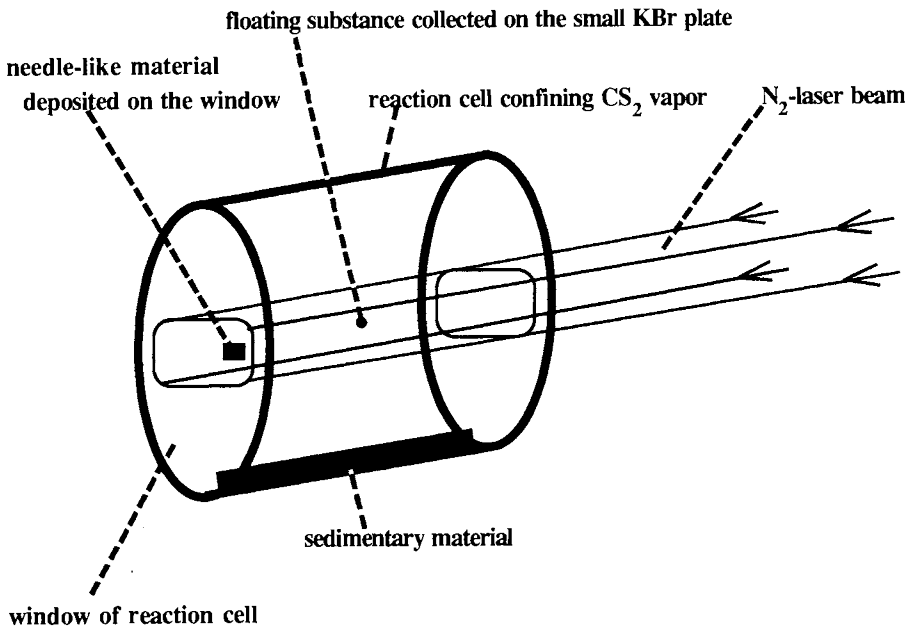

Fig.1. Schematic representation for the experimental set-up for the formation of the needle-like material deposited on the window surface of the reaction cell, the floating substance collected on the KBr plate placed in the center of the reaction cell, and the sediment on the bottom of the reaction cell.

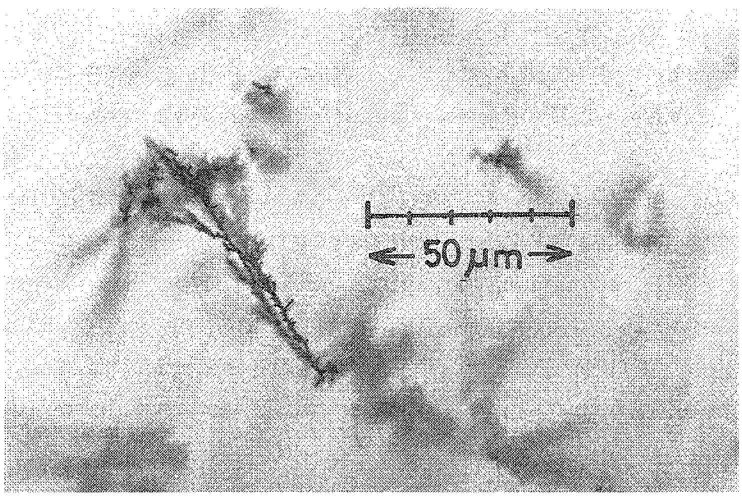

Fig.2. The optical microscope image of the needle-like material deposited on the window surface of the reaction cell. Three-dimensional veins-of-leaf clusters are formed.

small near the glass plate placed there. Hence the floating substance adhering to the glass plate put in the center of the reaction cell populates rather uniformly, and a veins-of-leaf cluster is not formed.

The fine ordered patterns of the DLP clusters might suggest a microcrystalline structure. Yet, X-ray diffraction experiments show that there is no evident peak indicating a crystalline structure; the DLP cluster is amorphous as well as the sedimentary material and the floating substance are.[11)]

In Fig.3, the infrared spectrum of the DLP cluster, spectrum 3, is compared with the spectra of the sediment and the floating substance, spectra 1 and 2, respectively. The intensity of the infrared spectrum of the DLP cluster is very weak like those of the floating substance and the sediment. This indicates that the DLP cluster also consists of fairly homonuclear bonds such that a local functional group is difficult to be defined, or are rather even in their atomic constitutions. The spectrum is rather similar to that of the floating substance; the sharp bands at 1960, 1385, 1260, 1110, 1068, 1020 cm^{-1}, and the broad bands in the region of 1600-1700, 1400-1500 cm^{-1} are commonly observed in both spectra. Hence the DLP cluster and the floating substance partly have common constituents; these constituents will be a mixture of carbon polymers, C_n, and sulfur polymers, S_n, as discussed in detail in our previous paper.[12)] Yet, it is significant that the broad band in the region of 800-1100 cm^{-1} in the spectrum of the DLP cluster is not observed in the spectra of the floating substance and the sediment. We estimate that this characteristic band is due to the C-C stretching and/or ring vibrations of carbon polymers;[15)] it should be difficult to assign this broad characteristic band to the characteristic modes of C-S polymers, since the intensity is extremely weak and the band frequency does not coincide with that of the C-S characteristic mode,

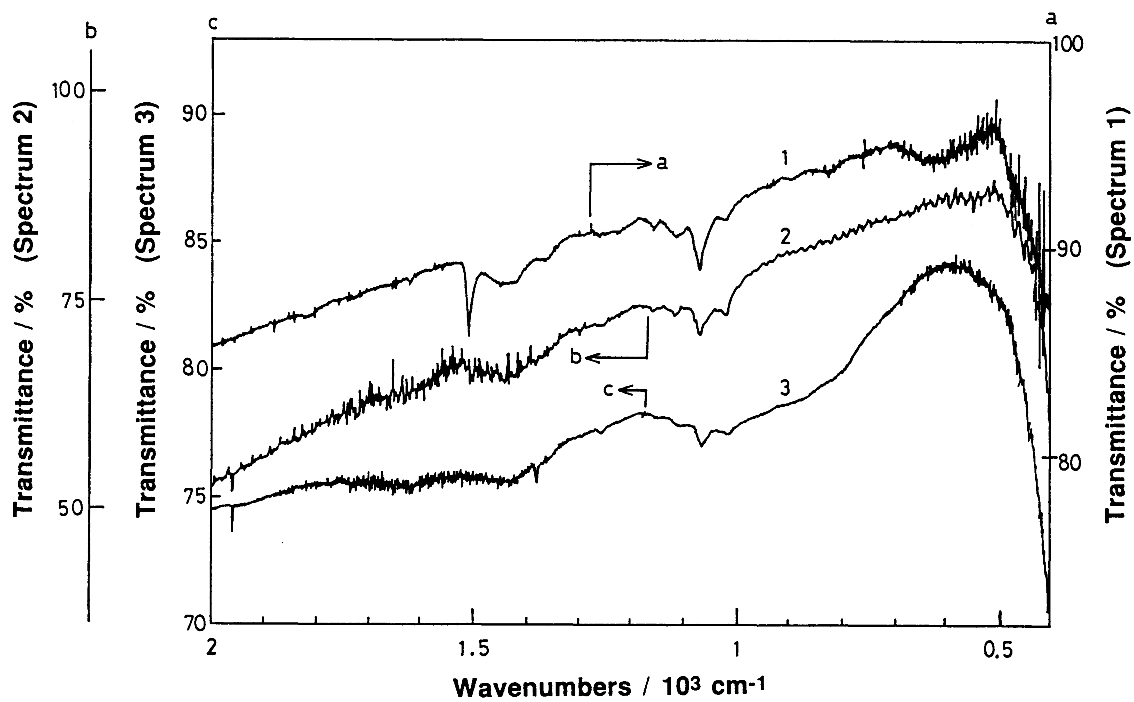

Fig.3. The infrared spectra of the sediment (spectrum 1), the floating substance (spectrum 2), and the needle-like material (spectrum 3). Vertical axes a, b, and c indicate the transmittances of spectra 1, 2, and 3, respectively. The samples were placed on KBr plates for infrared spectroscopy; each sample has a weight of about 100 μg.

which is 500-750 cm^{-1}.[15] Furthermore, the broad band around 1500 cm^{-1} is intense in the spectrum of the DLP cluster. This broad band will be assigned to the carbon-skeleton vibrations of carbon polymers.[12]

The visible-ultraviolet spectrum of the DLP clusters turns out to be very close to the spectra of the sedimentary material and the floating substance[12] except the interference effect caused by particles. Hence the electronic structure of the DLP cluster will be close to those of the sedimentary material and the floating substance; the DLP cluster also consists of a mixture of carbon polymers, C_n, and sulfur polymers, S_n, which have π-character, sp^2-hybrid bonds.

Finally, we would like to discuss the formation processes of DLP clusters. In computer simulations, the DLP-cluster formation is controlled only by the adhesion-species distribution, and the characteristics of the species are not taken into account except the adhesion strength.[13,14] Consequently, the DLP-cluster formation is not concerned by whether microcrystalline structures are constructed; whether the DLP-cluster formation is controlled by the chemical characteristics of adhesion species. However, in the present reaction system, we have observed the characteristic band in the infrared spectrum of the DLP cluster; it is not observed in the spectrum of the floating substance. This indicates that a selected species preferentially adheres to the cluster, or the adhesion species changes into another compound when it adheres to the cluster. Thus the present study points out the importance of the chemical characteristics of adhesion species in DLP-cluster formation.

The authors would like to thank Dr. T. Matsuzaki of Research Center of Mitsubishi Kasei Corp. for X-ray diffraction experiments, and Dr. H. Morita of Chiba University for his valuable comment.

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(Received November 7, 1991)