Deformation Vibration of SiOH

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When crystalline silica is ground into fine particles which have a particle size of about 1 μ, its surface is destroyed and its original structure is modified into an irregular one. On this layer, which is easily soluble in an aqueous alkaline solution, the silanol group is formed by the reaction between atmospheric water vapor and the Si–O– or Si– which is produced by the cleavage of the Si–O–Si bond. A parallel exists between the grinding process and the infrared absorption spectrum of the particle; i. e., the spectrum of the ground particle gives rise to a band at 950

cm^{-1} band, and the band group near 1100 cm^{-1} becomes more diffuse. The present author[1,2] has previously assigned the band near 1100 cm^{-1} to the SiO stretching vibration which appeared on the new surface layer and the band at 950 cm^{-1} to the SiOH deformation vibration. On the basis of the experimental finding that the band at 950 cm^{-1} diminishes or decreases in intensity by ethylation of the ground particle, his assignment has been considered to be correct[3]. Recently, however, Takamura et al.[4] assigned the band at 950 cm^{-1} to the SiO stretching vibration of the silicate structure which is produced on the new surface layer and the band near 1120 cm^{-1} to the SiOH deformation vibration on the basis of the results of the deuteration and other treatments of the particle. The experimental results described above can be explained according to the assignments made by Takamura et al. Ethylation of the SiOH of the silicate structure produces SiOEt, and then the SiO structure of the silicate decreases; therefore, the band at 950 cm^{-1} decreases in intensity. The fact that the ethylation is more difficult than the deuteration can be also explained, considering that the SiO in the silicate structure has an ionic bond character, while the SiO in SiOEt has a homopolar bond character and that the reaction from SiOH in the silicate structure to that in SiOEt must pass over a relatively high activated-energy level. Therefore, the present author wishes here to correct his assignment of the 950 cm^{-1} band to the SiO stretching vibration and the band near 1100 cm^{-1} to the SiOH deformation vibration.

Shimadzu[5] has found a resemblance between the infrared absorption bands near 1100 cm^{-1} of the leached particle, the size of which is less than 0.1 μ, and that of the ground particle, but he found no band at 950 cm^{-1} for the leached particle. The surface of the particle is a terminal structure of the SiO_2 frame, and, therefore, it normally consists of Si–O–H and Si–O–Si bonds, the former being particularly dominant. Fine particles have a larger surface area, and the SiOH group increases in proportion to the particle size. The leached particle apparently does not have a silicate structure which is easily soluble in an aqueous solution of sodium hydroxide. These facts are only explainable by the assignments made by Takamura et al. Though the structure of the surface layer of the particle which is considered to be silicate-like SiO by Takamura et al. should be further reexamined, their assignment of the SiOH deformation vibration is correct.

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1) H. Sakabe, K. Kawai, K. Koshi, R. Soda, A. Hamada, M. Shimadzu and H. Hayashi, *Bull. Nat. Inst. Ind. Health*, No. 4, 1 (1960).

2) R. Soda, This Bulletin, **34**, 1491 (1961).

3) R. Soda, presented at the 15th Annual Meeting of the Chemical Society of Japan, Kyoto, April, 1962.

4) T. Takamura, H. Yoshida and K. Inezuka, presented at the same meeting as above.

5) M. Shimadzu, unpublished data (in this Institute).