The recoveries of PL were between 90—104% and the coefficients of variation were between 1.21—4.30%, while the recovery of PLP added to human serum was only 63.3%, suggesting that some amount of PLP might be precipitated with denaturated protein. It is, therefore, favorable to determine PLP as PL after hydrolysis in order to obtain higher recovery. The enzymatic hydrolysis of PLP was examined with the same procedure reported by Takanashi, *et al.*[7] As shown in Table I, the recovery of PLP added to serum increased from 63.3% to 91.6% by using acid phosphatase solution obtained from potato. The separately determination of PL and PLP would be achieved by this method after SM-cellulose column separation with 0.01N acetic acid as described by Yamada, *et al.*[5]

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Electron Spin Resonance Study of γ-Irradiated H_2SO_4-SiO_2 System

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The SO_4^- radicals was formed in γ-irradiated H_2SO_4–SiO_2 system at −196°. The formation of the SO_3^- radicals are accompanied when γ-irradiation is carried out after heat-treatment at 500°, indicating that H_2SO_4 on SiO_2 is stable even at 500°.

The SO_4^- radicals are known to be formed in γ-irradiated sulfuric acid glasses.[2–5] On the other hand, the SO_3^- and SO_2^- radicals are formed besides the SO_4^- radicals in irradiated sulfates. However, the kinds of the radicals change with the sorts of the sulfates and irradiation in these cases.[6–10]

In the present study, the electron spin resonance (ESR) spectra of the γ-irradiated H_2SO_4–SiO_2 system were measured and compared with the above-mentioned reports. In addition, the effects of heat-treatment and the absorption of H_2O were examined.

The property of silica as a solid acid is well known. The silica treated with H_2SO_4 behaves as an another acid which shows a catalytic effect, for example, on the cracking of petroluem.[11]

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On the other hand, γ-irradiation increases the acidity of clay.[12] Therefore, it is interesting to study what kind of radical is formed in the H_2SO_4–SiO_2 system.

Experimental

H_2SO_4 (Wako Pure Chemical Industries, Ltd.) and 100 mesh $SiO_2 \cdot xH_2O$ (Mallinckrodt Chemical Works) are guaranteed and analytical reagents, respectively.

$SiO_2 \cdot xH_2O$ was immersed in 50% sulfuric acid and boiled for 5 hours. The mixture was cooled to room temperature and the $SiO_2 \cdot xH_2O$ was washed 5 times with distilled water, and then dried in a desiccator. The sample is described hereinafter as H_2SO_4-SiO_2.

Gamma irradiation from a ^{60}Co source was carried out at a dose rate of about 5×10^4 R/hr for 17 hours at $-196°$.

ESR spectra were measured with a Japan Electron Optics Laboratory Model JES-3BS.X Spectrometer (X-band) with 100 kHz field modulation.

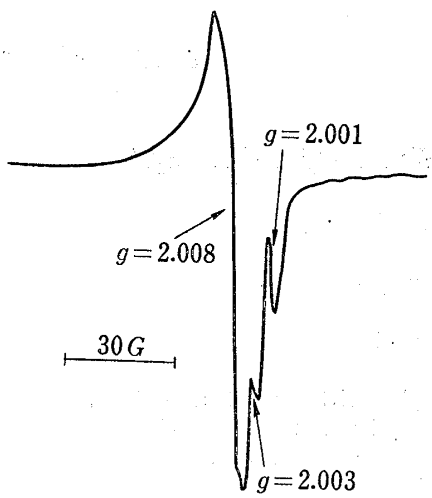

Fig. 1. ESR Spectrum of $SiO \cdot xH_2O$ at $-196°$, γ-Irradiated after Heat-treatment at 500° (gain 2.0×100)

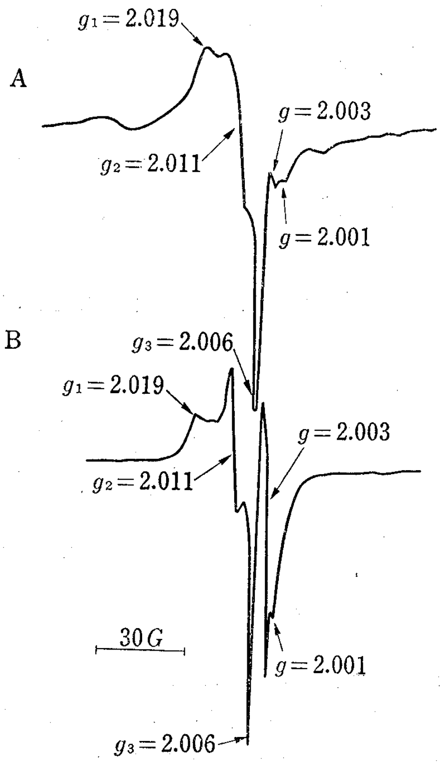

Fig. 2. ESR Spectra of γ-Irradiated H_2SO_4–SiO_2 at $-196°$, (A): Non-heat-treated (gain 6.3×10), (B): Heat-treated at 500° (gain 1.4×100)

Results and Discussion

Figure 1 shows the ESR spectrum of $SiO_2 \cdot xH_2O$ γ-irradiated at $-196°$ after heat-treatment at 500° for 5 hours. It is well known that the spectra of silica depends on the ways of preparation and impurities. The spectrum in Fig. 1 consists of three absorption lines and is very similar to that reported by Kinell, *et al.*[13] According to ref. 13, the absorption at $g=2.001$ appearing also in γ-irradiated quartz and fused silica is attributed to the electrons trapped in an oxygen vacancy in the SiO_2 network. The absorption at $g=2.003$ is probably due to trapped electrons, but the site is not clear. The strong and asymmetric absorption centered at $g=2.008$ is attributed to the holes trapped in a non-bridging oxygen formed by hydrogen

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rupture of the silanol group on the surface. These absorption lines almost disappeared when the sample was kept for a day at room temperature.

Figure 2-A shows the ESR spectrum of H_2SO_4–SiO_2 evacuated at room temperature and γ-irradiated at $-196°$. Two lines at $g=2.001$ and $g=2.003$ are attributable to the trapped electrons as in the case of $SiO_2 \cdot xH_2O$. The strong absorption in the low field side differs from that of the hole trapped at the surface oxygen. If the spectrum comes from only one species, asymmetric line shape is due to the anisotropic g value ($g_1=2.019$, $g_2=2.011$, $g_3=2.006$). The values are nearly equal to those of the SO_4^- radicals ($g_1=2.0189$, $g_2=2.0130$, $g_3=2.0053$) formed in γ-irradiated frozen aqueous sulfuric acid glasses.[3] These radicals disappeared when the sample was kept at room temperature for a day.

Figure 2-B shows the ESR spectrum of H_2SO_4–SiO_2 γ-irradiated and measured at $-196°$ after heat-treatment at 500° for 5 hours. The strong absorption line in the low field side is somewhat different from that in Fig. 2-A. However, the g values of the radicals are exactly equal. Furtheremore, the sample adsorbed H_2O in contact with the saturated vapor of H_2O at room temperature after heat-treatment at 500° and then γ-irradiated at $-196°$ shows an ESR spectrum very similar to that in Fig. 2-A with respect to the intensity and the line shape. These facts suggest that H_2SO_4 on SiO_2 is stable even at 500° in contrast to H_2SO_4 which decomposes at 290° and the difference between the spectra in Fig. 2-A and 2-B comes from the effect of adsorbed H_2O. Considering the facts that H_2SO_4 is not destroyed by heat-treatment at 500° and the g values are equal, both absorptions in the low field side in Fig. 2-A and 2-B can be attributed to the SO_4^- radicals. The difference in line shape may be due to the change of the environment resulting from dehydration.

Besides the absorption of the SO_4^- radicals, a strong and sharp absorption at $g=2.003$ was found in Fig. 2-B, which is much stronger than that of $SiO_2 \cdot xH_2O$. It is possible to consider that the new site for electron trapping was produced or another type of sulfur oxide radicals was formed by γ-irradiation. In the sulfur oxide radicals, the SO_3^- radical has a nearly isotropic g value and shows a singlet near at $g=2.003$. This radical is known to be stable even at 200°.[9] The absorption intensity of the SO_4^- radicals in Fig. 2-B decreased when the sample was kept for a day at room temperature. On the contrary, the absorption at $g=2.003$ became stronger. It has been reported that the SO_4^- radicals formed in the sulfate by γ-irradiation at $-196°$ decomposes into the SO_3^- radicals at room temperature.[7] From these results, the absorption at $g=2.003$ is attributable to the SO_3^- radicals. The radicals did not decay by heat-treatment at 100° for 7 hours. The adsorbed H_2O makes the formation of the SO_3^- radicals difficult is consistent with the fact that the SO_3^- radicals were not found in γ-irradiated aqueous sulfuric acid glasses.

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