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THE VIBRATIONAL SPECTRA OF α, β, AND γ-PICOLINES ADSORBED ON AEROSIL SILICA

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The vibrational spectra of α, β, and γ-picolines adsorbed on aerosil silica were measured in the regions of 2800-4000 cm^{-1}, 1300-1650 cm^{-1}, and 950-1100 cm^{-1}. At high coverage, two kinds of the surface species were found, which were assignable to the liquid-like species and the hydrogen-bonded species persisting at low coverage.

It has been shown that the Raman spectroscopy is the useful technique for the study of the gas-solid interface[1-4], since the Raman intensities of many adsorbates are sufficiently weak. On the other hand, the infrared spectroscopy has an advantage that the structure of surface OH groups can be easily identified by the strong OH stretching band, although the adsorbates show strong background spectra in the finger print region[5]. However, in previous works on the interface, both of the techniques have been rarely employed simultaneously and the frequency region observed was limited[2].

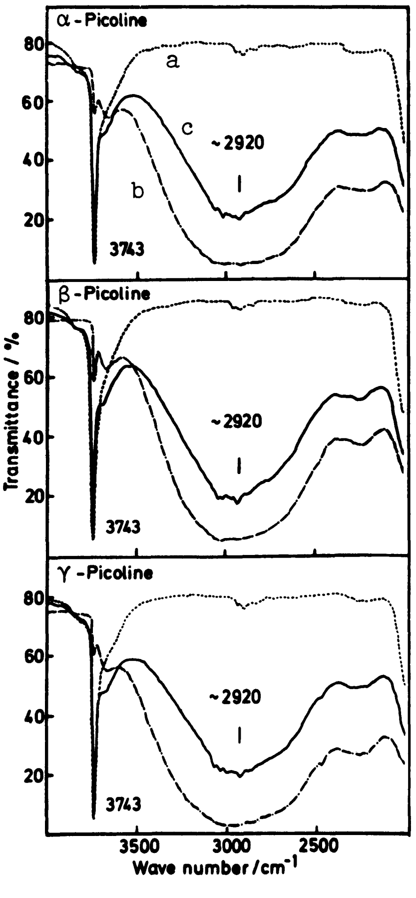

Fig. 1. Infrared spectra of adsorbed picolines in the 2100-4000 cm^{-1} region.

In the present work, in order to investigate the effects of the methyl group substituted to pyridine, the vibrational spectra of α, β, and γ-picolines were studied in the frequency regions of 2800-4000 cm^{-1} (infrared and Raman spectra), 1300-1650 cm^{-1}(infrared and Raman spectra), and 950-1100 cm^{-1}(Raman spectra) using both the techniques.

The Raman spectra of the adsorbed species were recorded on a JEOL JRS-400D laser Raman spectrometer fitted with a Coherent model CR-2 Argon-ion laser using an interference filter. The vacuum Raman cell with a stopcock consists of a quartz tube closed by a flat at one end. The aerosil silica supplied by Nippon Aerosil Co. Ltd. with the specific surface area of 380 m^2/g was used in the form of broken disks into powders. The sample of silica contained in the Raman cell was evacuated to 10^{-3} Torr at 550°C for four hours, followed by an oxygen treatment (550°C, 700 Torr) for six hours to remove any organic contaminates, and then evacuated to 10^{-3} Torr at 550°C for two hours[3]. After the system was allowed to cool at room temperature, picolines were introduced into the system.

The Raman spectra were also obtained for the aqueous solution and chloroform solution of the hydrochlorides (*ca.* 0.5 mol/l). The infrared spectra of the adsorbed species at room temperature were recorded on a Perkin-Elmer 621 spectrophotometer using *in situ* cell conventionally designed. The disks of 20 mm dia. of aerosil silica (13mg /cm^2) compressed under a pressure of 10 tons/sq. in. were used for the measurements, after the half-period pretreatment used in the Raman measurements.

The 2800-4000 cm^{-1} region. The infrared spectra in this region are shown in Fig. 1 ; (a) for the silica, (b) for the silica exposed to the picoline vapors, till the band at 3743 cm^{-1} almost disappears, and (c) after evacuation to 10^{-3} Torr for thirty minutes. The band of free silanols at 3743 cm^{-1} decreased its intensity upon adsorption of the picolines and then, the broad bands at *ca.*2920 cm^{-1} appeared, indicating the interaction between the surface silanols and picolines. The CH stretching bands, however, were hardly observed owing to the intense band at *ca.* 2920 cm^{-1}. The Raman spectra of picolines adsorbed on the silica in the 2800-3150 cm^{-1} region are shown in Fig. 2 ; (a) high coverage (*ca.* 30A^2/molecule) and (b) low coverage (*ca.* 80A^2/molecule). For the pyridine adsorbed on silica[1-4], in order to distinguish the surface species (the hydrogen-bonded species, pyridinium ion, and liquid-like species), the comparison of the spectra of the adsorbed species has been made with those of the aqueous solution, typical salts, and pure liquid. In comparison of the spectra of the adsorbed picolines with those of the pure liquids (spectra e), the Raman lines in the spectra (a) disappeared at low coverage may be due to the liquid-like picolines on the surface, indicating the existence of the two kinds of surface species at high coverage. The spectra (b) at low coverage do not resemble with those of the pure liquids and the salts (spectra d) but resemble with those of the aqueous solutions (spectra c).

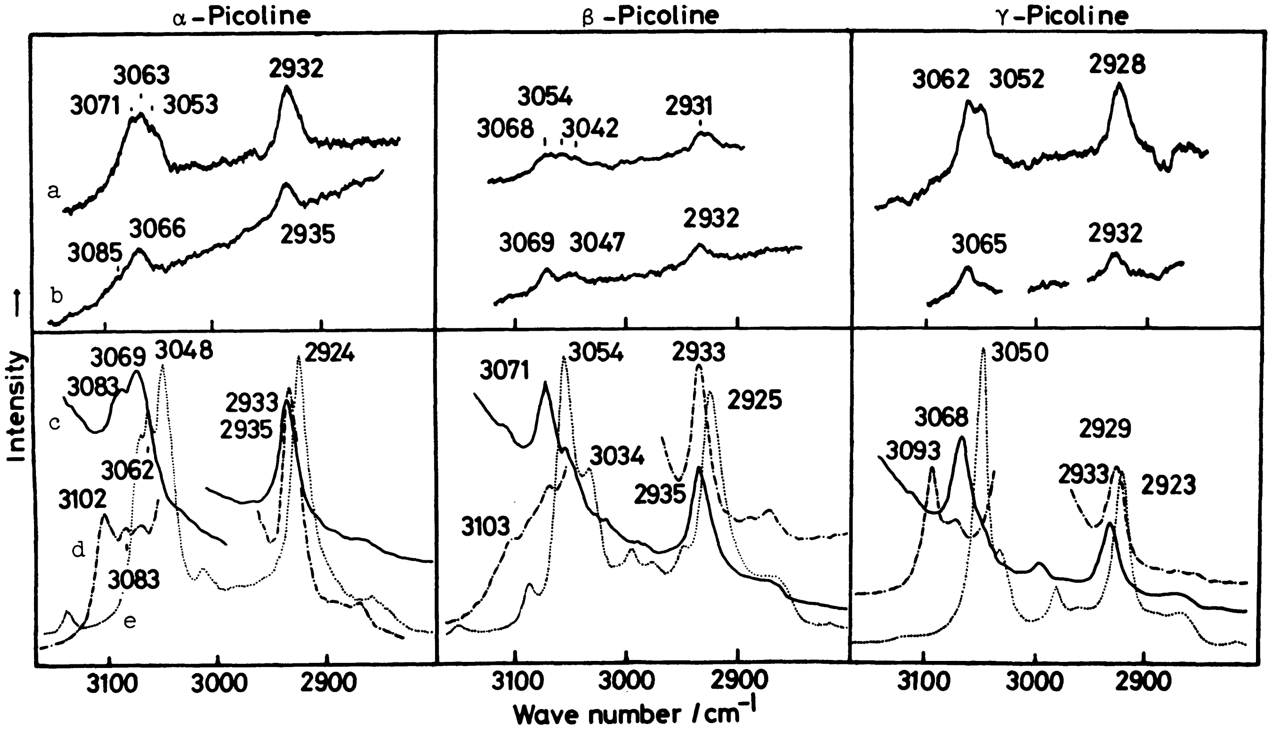

Fig. 2. The Raman spectra of picolines in the 2800-3150 cm^{-1} region.

The 1300-1650 cm^{-1} region. The infrared and Raman spectra are shown in Fig. 3; the notations (a), (b), and (c) in the figure are the same as those in Fig. 1. and the Raman spectra (d) show those of the adsorbed species at low coverage for β-picoline and at high coverage for α and γ-picolines. The infrared frequencies observed (spectra b) agree with the Raman frequencies within ± 3 cm^{-1}. Apparently, the S/N ratios of the infrared spectra are better than those of the Raman spectra. The existence of two kinds of surface species are not so obvious from this frequency region, since the spectra of the adsorbed species do not so much differ from those of the pure liquids (spectra g). However, the spectra of the aqueous solutions (spectra e) apparently differ from those of the salt (spectra f) but correspond with those of surface species.

The 950-1100 cm^{-1} region. Only the Raman spectra could be obtained for this region, since the strong background was observed in the infrared spectra. The Raman spectra obtained are shown in Fig. 4 ; (a) and (b) at high and low coverages respectively. In this region, two Raman lines were observed for the pure liquids (spectra e). On the other hand, three lines were observed for the adsorbed species at high coverage. One of them disappeared at low coverage, clearly indicating the existence of two kinds of the surface species. Apparently, the Raman line disappeared is due to the liquid-like picolines and the remaining two lines at low coverage could be assigned to the adsorbed species interacted with surface silanols. In comparison of the spectra of the adsorbed species at low coverage with those of the aqueous solutions (spectra c), the salts (spectra d), and the pure liquids (spectra e), the spectra of the adsorbed β-picoline correspond with those of aqueous solution both in relative intensity and in frequency. On the other hand, for α-picoline, the lower-frequency Raman line of the adsorbed species coincides with that of the salt and for γ-picoline the relative intensity dose not resemble with that of

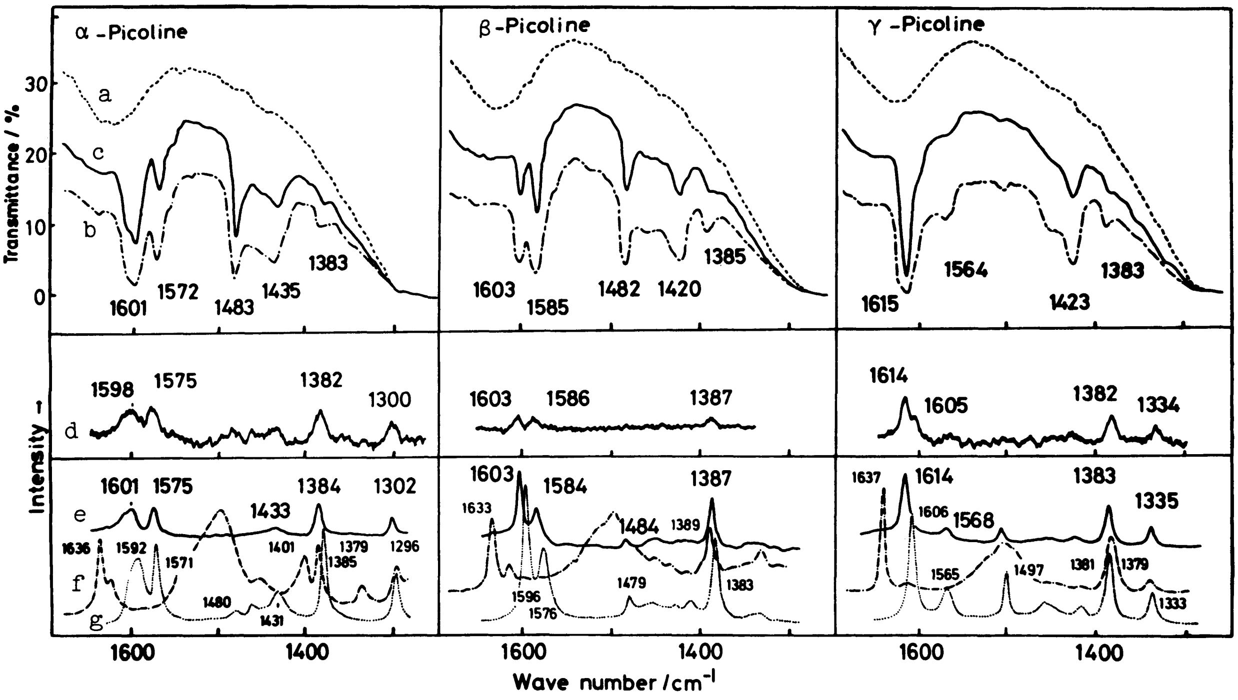

Fig. 3. The infrared and Raman spectra of picolines in the 1300-1650 cm^{-1} region.

the aqueous solution but resemble with that of the salt, suggesting that the mutual interactions of α or γ-picoline with silica surface is that in the medium state of the aqueous solution and the salt.

In conclusion, it is confirmed that the adsorbed picolines at low coverage form hydrogen bonds with the surface silanols, since the infrared band of the free silanols at 3743 cm^{-1} decreases its intensity on adsorption with newly appearing the band of the interacted silanols at the lower-frequency region and the Raman spectra of the adsorbed species at low coverage correspond with those of the aqueous solution not only in the 2800-3150 cm^{-1} but also in the 1300-1650 cm^{-1} regions. The infrared bands of the interacted silanols appeared at *ca.* 2920 cm^{-1} for all of the picolines suggest that the ability of the hydrogen bonding may be roughly equal for them. However, the Raman spectra of the 950-1100 cm^{-1} region indicate that the ability is slightly different among them; the hydrogen bonds of α and γ-picolines with the surface silanols may have partly the character of the picolinium ions and, on the other hand, that of β-picoline with silanols may be just analogous to that in the aqueous solution. Thus, on the mechanism of the adsorption of the picolines, the electronic density on the nitrogen atoms may take more important roles rather than the steric hindrance of the methyl group, on the basis of the ability of the hydrogen bonding among the picolines. For the steric hindrance of methyl groups substituted to pyridine on adsorption, the study of the dimethyl pyridine adsorbed are in progress.

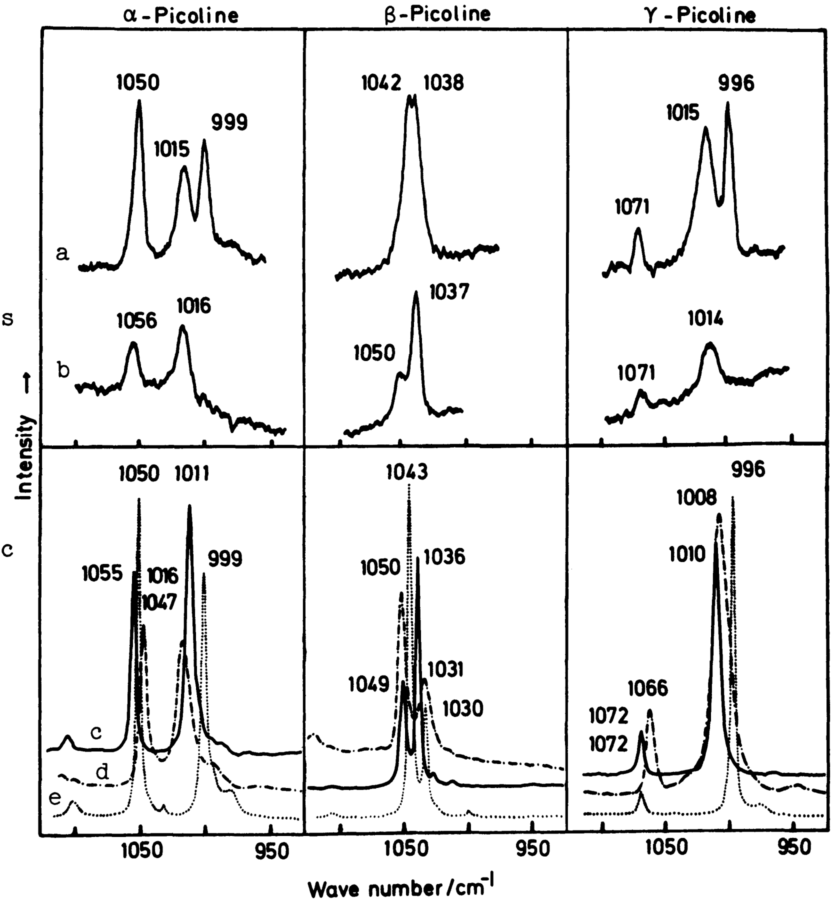

Fig. 4. The Raman spectra of picolines in the 950-1100 cm^{-1}.

References

1) R. O. Kagel, *J. Phys. Chem.*, 74, 4518 (1970).

2) P. J. Hendra, J. R. Horder, and E. J. Loader, *J. Chem. Soc. (A)*, 1766 (1971); P. J. Hendra and E. J. Loader, *Trans. Faraday Soc.*, 67, 828 (1971); P. J. Hendra, I. M. Turner, E. J. Loader, and M. Stacey, *J. Phys. Chem.*, 78, 300 (1974).

3) T. Nagasao and H. Yamada, *Chem. Lett.*, 1045 (1974).

4) T. A. Egerton, A. H. Hardin, Y. Kozirovski, and N. Sheppard, *J. Catal.*, 32, 343 (1974).

5) L. H. Little, *Infrared Spectra of Adsorbed Species*, Academic Press, N. Y. (1966).

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