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RESONANCE RAMAN SPECTRA OF CARBONIUM IONS ADSORBED ON POROUS VYCOR GLASS

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When 1,1-diphenylethylene(DPE) was adsorbed on porous Vycor glass, some unstable intermediates, blue, green and yellow species, were produced. The resonance Raman spectra of the green and yellow species were observed. The green species showed three new bands at 2975, 2930 and 2873 cm^{-1} and the yellow species one at 2930 cm^{-1}. The observed Raman spectra have confirmed the existence of two kinds of carbonium ions.

Recently it has become clear that laser Raman spectroscopy can be applied effectively to the study of adsorbed species.[1-6] Raman lines from the adsorbed species, however, generally appear with low S:N ratio, because the number of surface species in the sample is quite small. In order to detect a small amount of adsorbed species and elucidate the interaction between adsorbents and adsorbates, we have applied the resonance Raman effect to studies of silica surfaces.[7] The resonance Raman spectrum of iodine adsorbed on silicas has been successfully obtained and this technique is proving to be of value to surface studies.

It is known that some unstable intermediates can be produced when 1,1-diphenylethylene(DPE) is adsorbed on a catalyzer, silica-alumina. They have been investigated by measuring the electronic and ESR spectra and explained in connection with a radical ion and a classical carbonium ion.[8,9] Since a color development similar to that for DPE adsorbed on silica-alumina can be observed for DPE adsorbed on porous Vycor glass(PVG), the existence of unstable intermediates is also expected on silicas. PVG is the most convenient adsorbent for Raman measurements, and its pretreatment has been throughly studied.[3,5,6]

Porous Vycor glass(PVG) from Corning Glass Works, No.7930 (a plate 1 mm thick) was used as adsorbent. The pretreatment for cleaning surfaces and eliminating of fluorescence was performed in the way described in previous papers.[6,7] Guaranteed reagent of 1,1-diphenylethylene(DPE) was obtained from the Wako Chemical Co. and was used without further purification.

A pyrex or quartz cell, with a side tube, contained the PVG which was already pretreated and was ca. 10 X 20 X 1 mm large, and liquid DPE in its side tube. The cell was connected to a vacuum line and the DPE was cooled to liquid nitrogen temperature. After the PVG was heated at 400°C for 4 hrs, both the PVG and the DPE were kept at 25°C. The vapor of DPE was gradually adsorbed on the PVG and the sample appeared blue. The blue sample gradually changed to green. When the PVG was immersed in the liquid DPE, the change in color was accelerated and the sample appeared green in about 30 minutes. The green sample gradually changed to yellow in several days, and finally became reddish brown.

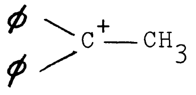
The Raman spectrum was measured for each colored sample. The laser beam, parallel to the surface of the PVG, irradiated the sample from the bottom of the cell, and the scattered light was gathered in a direction perpendicular to the incident beam. A Jasco R-300 Raman spectrophotometer with a JEOL, JLG-04 argon ion laser was used. In order to avoid the changing of the samples by the irradiation of the laser beam, the power of the laser used was kept as low as possible. The spectral slit-widths used were 8 ~ 17 cm^{-1}.

For the red sample little change due to irradiation by the laser beam was observed, while the blue, green and yellow samples began to fade upon irradiation. When the green and yellow samples, however, were immersed in DPE liquid, the fading became so slow that Raman measurements were possible.

The observed Raman spectra for the green, yellow and red samples are shown in Fig. 1. For the green sample, three new bands are found at 2975 cm^{-1} (partly overlapping with a DPE band), 2930 cm^{-1} and 2873 cm^{-1}, and the strong bands in the ~1600 cm^{-1} region increase in intensity remarkably, especially with 457.9 nm excitation. On the other hand, the 2873 cm^{-1} band does not appear for the yellow sample, though the 2930 cm^{-1} band is clearly observed. For the red sample both the 2930 cm^{-1} and 2873 cm^{-1} bands disappear, and instead a strong new peak at 1595 cm^{-1} appears. In Fig.1, for the larger spectral slit-widths than 16 cm^{-1} the doublet at ~1600 cm^{-1} can not be resolved.

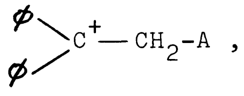
The Raman spectra obtained for the green, yellow and red samples are interpreted as the spectra of the liquid DPE overlapping with some new bands which appeared on adsorption of DPE on the PVG surface. The three new bands at 2975, 2930 and 2873 cm^{-1} are ascribed to certain intermediates produced by adsorption of DPE on the PVG, because they appear in the green and yellow samples but not in the red sample. Since the band at 2930 cm^{-1} behaves differently from the band at 2873 cm^{-1}, two kinds of intermediates must exist. The bands at 2975 cm^{-1} and 2873 cm^{-1} are assigned respectively to -CH_3 antisymmetric and symmetric stretching vibrations, and the band at 2930 cm^{-1} to -CH_2 antisymmetric stretching vibration.

Since a similar color development to that for DPE adsorbed on silica-alumina was observed for the present samples on PVG, the existence of the unstable intermediates similar to those on silica-alumina8,9) can be expected. Based on the observed new bands, the intermediates can be considered to be following carbonium ions,



(I)

and



(II)

where A means the adsorbent (a Si or B atom). The green sample contains both carbonium ions, and the yellow sample certainly has the latter. These structures were also suggested by Leftin et al8) for the green species on silica-alumina.

The electronic absorption spectra were measured for the same samples as used for the Raman spectra. A Cary Model 14 spectrophotometer with the quartz cell was used. The blue and green samples showed absorption maxima at 612 nm and 430 nm,

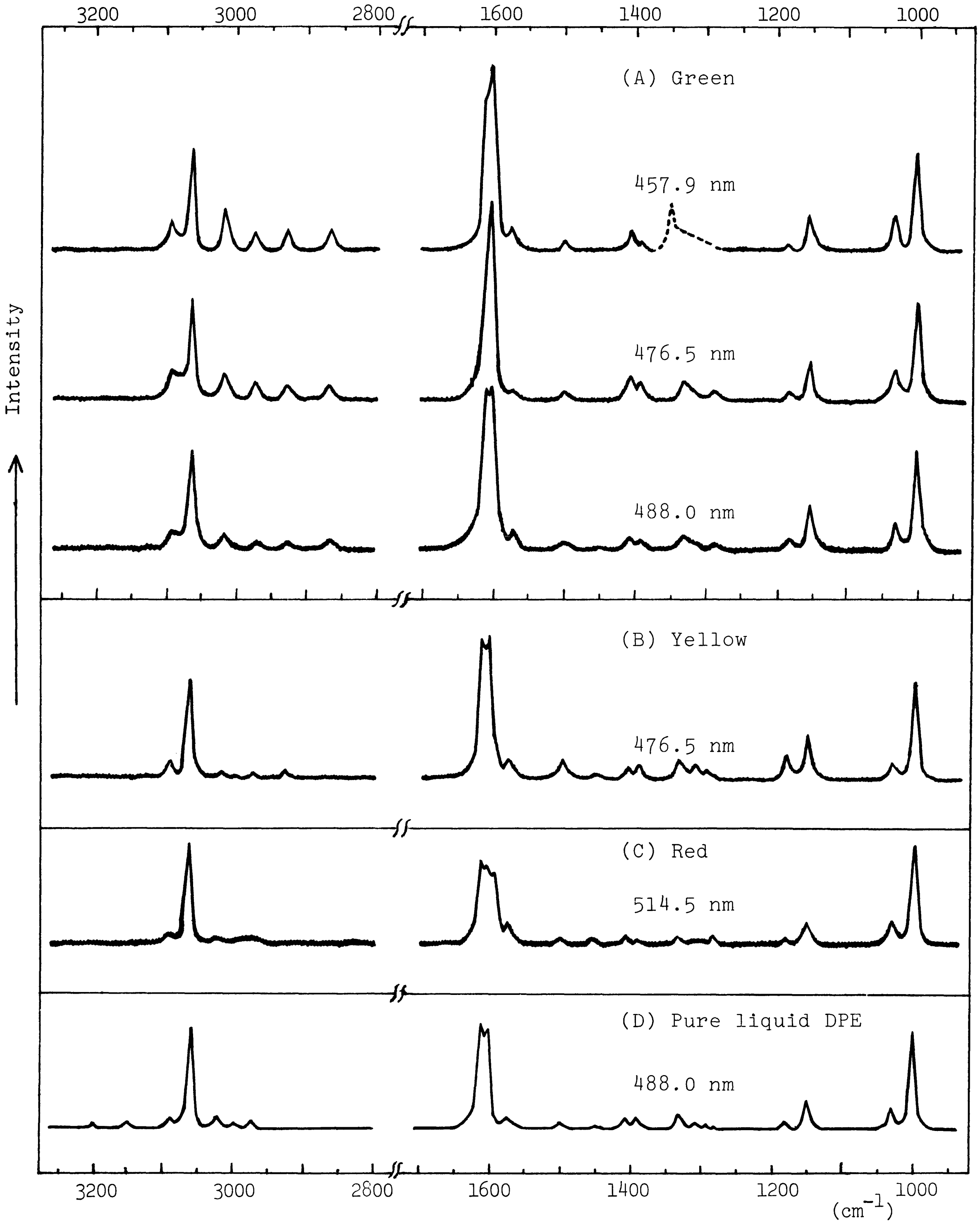


Fig. 1. Raman spectra of DPE adsorbed on PVG, (A) green sample, (B) yellow sample, (C) red sample and (D) DPE in the liquid phase.

respectively. These maxima correspond to those observed for the blue and green species adsorbed on silica-alumina.$^{8)}$ The yellow sample showed an absorption band at 503 nm.

Since the relative intensities of Raman bands for the green and yellow samples depend on the wavelength of excitation, the resonance Raman effect is certainly indicated. Because the excitations at 457.9 nm and 476.5 nm for the green sample are in the absorption region, the resonance effect is considerably larger for these cases and contributes advantageously to the detection of the small amount of the adsorbed species. Even though the concentration of the carbonium ions might be small, the Raman spectra of the yellow sample can be observed with strong enhancement, because the absorption band at 503 nm covers almost all the Ar^+ laser lines.

The ESR spectra for the colored samples were measured by use of a JEOL-JES 3B apparatus. Only the blue sample showed a very weak ESR signal. Since the electronic and ESR spectra for the blue sample agree well with those observed for the blue species adsorbed on silica-alumina,[8,9] the same species as that on silica-alumina might be involved. It may be interpreted as a cation radical, $[(C_6H_5)_2C\dot{-}CH_2]^{+}$, as suggested by Leftin et al[8], which may convert to the carbonium ion (II). Tne Raman spectrum characteristic of the blue species, however, could not be observed with the Ar^+ laser excitation.

These intermediates, the carbonium ions and the cation radical, are decomposed in the red sample by the formation of stable reaction products, which might be dissolved in the liquid phase or physically adsorbed on the PVG. The main products have been found to be the initial compound, DPE, and benzophenone from the infrared measurements. The new strong band at 1595 cm^{-1} is considered to be due to some π-complexes formed with the products.

It can definitely be said that the sensitivity of these resonance Raman spectra is comparable with that of the electronic absorption spectra. Consequently from the vibrational spectra one can obtain detailed information about the structure of a small amount of an adsorbed species.

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