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Surface Acidity of Solid Acids. Ultraviolet Spectroscopic Investigation of Adsorbed Pyridine

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The ultraviolet spectra of adsorbed pyridine has been studied on several acidic solids (SiO_2, η-Al_2O_3, NaX). The adsorbed pyridine had the π–π^* band slightly shifted to longer wavelength from that of pyridine vapor. The bands of protonated pyridine and those of hydrogen bonded pyridine showed characteristic vibrational structure with a peak maximum at 256 nm. Pyridine coordinated on η-alumina gave a broad band at 258 nm. In the case of NaX zeolite, three kinds of adsorbed species were found. The adsorbed states are discussed.

INTRODUCTION

The nature of the acidic sites of solid catalysts have been investigated by various methods for the past two decades (*1*). As pyridine is a relatively strong base ($pK_b \sim 9$), the amount of pyridine chemisorbed at high temperature has been used as a measure of determining acidity (*2*), and the use of infrared spectra of adsorbed pyridine to distinguish between Brønsted and Lewis acid sites is now well established (*3–5*). There has also been some work (*6*) concerning the π–π^* band of adsorbed pyridine by the observation of ultraviolet spectra. The shift of the position of the π–π^* band of adsorbed pyridine on acidic solids depends on the bond between pyridine and acid sites, and ultraviolet spectra afford a highly sensitive detection of acid sites due to the large extinction coefficient of the π–π^* band. Pyridine vapor shows a π–π^* band (^1L_b) with a vibrational structure in which the peak maximum is located at 249.5 nm. Robin *et al.* (*6*) reported that the corresponding band of adsorbed pyridine on suspending silicic acid in cyclohexene shows a shift to longer wavelength, the band occurring at almost the same position as that of protonated pyridine in acidic aqueous solution. This result was interpreted as due to the hydrogen bond between the nitrogen atom of the pyridine and a hydroxyl group on silicic acid. Kishi and Ikeda (*7*) reported that pyridine adsorbed on Ti, Fe, and Ni film showed a π–π^* band at around 260 nm and the band at 297 nm on Fe was assigned as a charge transfer band. In this paper we report the ultraviolet spectra of adsorbed pyridine on some typical acidic solids and discuss their interpretation.

EXPERIMENTAL

Materials

Two kinds of silica gel were prepared. One was Cab-O-Sil-M-5 silica. The sample was calcined in air at 500°C for 6 hr. The surface area was 182 m^2/g and no stronger acid sites were detected than those corresponding to a Ho value (indicator pK_a) of +4.8. Another silica gel was prepared by hydrolysis of ethyl silicate with water at 100°C. Ethyl silicate was purified by double distillation from a commercial guaranteed reagent. The sample was calcined in air at 500°C for 6 hr and the surface area was 423 m^2/g. A Ho value of +3.3 was observed. η-Alumina was prepared by calcination of bayerite in a nitrogen stream at 500°C for 6 hr. Bayerite was obtained by hydrolysis of aluminum-isopropoxide furnished as Extra Pure Reagent grade from Nakarai Chemicals Ltd. The surface area was 256 m^2/g. The X-ray diffraction patterns showed the typical patterns of η-alumina. Sodium X zeolite was Linde 13X with no binder. The surface area was 840 m^2/g. Pyridine was Guaranteed Reagent grade from Nakarai Chemicals Ltd. It was further dried over activated 3A zeolite after fractional distillation in a vacuum.

Procedure

The spectra of the samples were determined as diffuse reflectance spectra on a Beckman DK-2A spectrophotometer equipped with a standard reflectance attachment. The absorbance is represented by the logarithm of the Schuster–Kubelka–Munk function, $F(R_\infty) = (1 - R_\infty)^2/2R$, where R_∞ is the reflectance measured against magnesium oxide. The sample was placed in a vacuum cell with a quartz window and evacuated for 1 hr. The temperature was then slowly raised to 400°C and maintained for 5 hr ($\sim 10^{-5}$ Torr). The sample was then cooled to room temperature and allowed to equilibrate with pyridine at 3 Torr for 1 hr. The gas phase pyridine and adsorbed pyridine were then removed by evacuation for 2 hr at various temperatures. After cooling to room temperature, the spectrum was measured.

RESULTS AND DISCUSSION

Pyridine on Silica

The ultraviolet spectra of pyridine on Cab-O-Sil silica are shown in Fig. 1, and the band positions are summarized in Table 1. When evacuated at room temperature, the π–π^* band of the adsorbed species gave the vibrational structure to longer wavelength from that of pyridine vapor. The

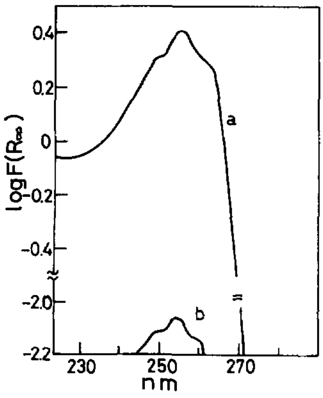

FIG. 1. Reflectance spectra of pyridine adsorbed on Cab-O-Sil silica. (a) After evacuation at room temperature; (b) after evacuation at 150°C.

TABLE 1

ULTRAVIOLET BANDS OF PYRIDINE IN VARIOUS STATES

Sample		Wavelength (nm)				
(1) Gas		260.5	254	249.5[a]	244.5	239
(2) Protonated pyridine in aqueous solution		262	256[a]	~245		
(3) Adsorbed on						
Cab-O-Sil silica	A	262	256[a]	250		
	B	262	256[a]	250		
Silica by hydrolysis of ethyl silicate	A	261	256			
	C	261	256[a]	250	244	
	D	261	256[a]	250		
η-alumina	C	258[a]				
	D	258[a]				
NaX	A	265[a]				
	C	260[a]				
	D	261	256[a]	250		

[a] The strongest peak of the pyridine band; A, after evacuation at room temperature; B, after evacuation at 150°C; C, after evacuation at 250°C; D, after evacuation at 400°C.

positions and shapes of these spectra are similar to those of adsorbed pyridine on silicic acid (*6*) and that of protonated pyridine in acidic aqueous solution. This is also attributed to the hydrogen bond between the nitrogen atom of pyridine and silanol groups on Cab-O-Sil silica. The species were mostly removed by pumping at 150°C. This indicates that the species were weakly adsorbed only by hydrogen bonds, and neither Brønsted nor Lewis acid sites exist on the surface. Our experimental results agree approximately with those of Parry (*3*) deduced from the infrared spectra of adsorbed pyridine on Cab-O-Sil silica. He showed that pyridine on silica was held only by a hydrogen bond.

Figure 2 shows the spectra of adsorbed pyridine on silica prepared by hydrolysis of ethyl silicate with water. When evacuated at room temperature, the adsorbed species gave two broad bands at around 261 nm and 256 nm. The spectra were quite different from that of Cab-O-Sil silica. On evacuation at 250°C, the intensity of the band decreased considerably. The positions and shape of the spectra are then quite similar to that of hydrogen bonded pyridine seen in Fig. 1. It is very difficult to distinguish between hydrogen bonded and protonated pyridine by the spectra because of the similarity of their bands. However, it seems to be very likely that the predominating species adsorbed on the surface are protonated pyridine, because this sample of silica has stronger acid sites (Ho = +3.3) than Cab-O-Sil silica (Ho = +4.8). The bands obtained after evacuation at room temperature indicate the existence of the hydrogen bonded pyridine and other unidentified types of pyridine. The latter species are also very unstable.

Pyridine on η-alumina

Figure 3 shows the spectra of adsorbed pyridine on η-alumina. When it was evacuated at 250°C, the adsorbed species gave a band with a peak maximum at 258 nm, which remained at the same position even after evacuation at 400°C. The adsorbed species showed the π–π^* band shifted slightly to longer wavelength than that of protonated pyridine and the species are held strongly on the surface. Parry (*3*) showed from the infrared spectra of chemisorbed pyridine that η-alumina contained only Lewis acid sites and no protonic acid sites. Pines and Haag (*8*) also concluded that alumina displayed Lewis acidity, using various indicators. So, from the results described above, the broad band observed at around 258 nm should be explained as due to pyridine coordinated with the nitrogen atom on Lewis acid sites (aluminum ion). The position of the band is very close to

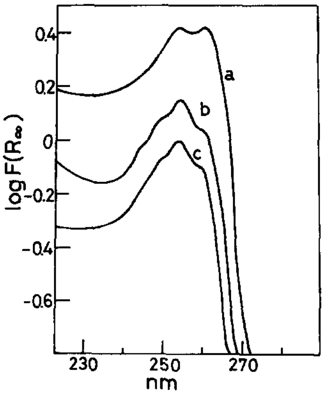

FIG. 2. Reflectance spectra of pyridine adsorbed on silica prepared by hydrolysis of ethyl silicate with water. (a) After evacuation at room temperature; (b) after evacuation at 250°C; (c) after evacuation at 400°C.

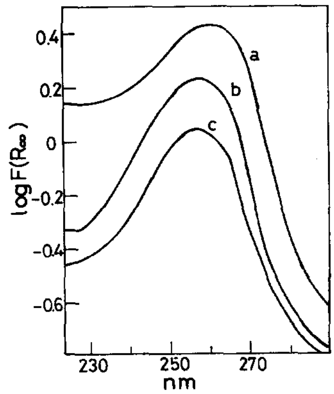

FIG. 3. Reflectance spectra of pyridine adsorbed on η-alumina. (a) After evacuation at room temperature; (b) after evacuation at 250°C; (c) after evacuation at 400°C.

that which indicates hydrogen bonded or protonated pyridine. Therefore, it is very difficult to distinguish from the band whether Brønsted acid sites exist on η-alumina.

Pyridine on NaX

Figure 4 shows the spectra of adsorbed pyridine on NaX after evacuation at various temperatures. When evacuated at room temperature, the adsorbed pyridine gave a broad band at 265 nm. By evacuation at 250°C the band shifted slightly to shorter wavelength at 260 nm. By further evacuation at 400°C, the intensity of the band decreased. The change of the spectra by evacuation indicates the existence of several types of acid sites on the surface. Hence, the broad band is made up of the overlap of individual spectra.

Although the species with the peak maximum at 265 nm were easily removed by evacuation, they do show absorption with the largest wavelength shift (compared to pyridine vapor) of all those observed for adsorbed pyridine on the solid surfaces. It is quite difficult to identify the mode of this adsorbed species. However, the observed facts, that is, weak absorption with the largest band shift seem to be characteristic of π-bonding by accepting p_π electrons of the ring, rather than of σ-bonding with lone pair electrons of pyridine. The remaining species after evacuation at 250°C are held relatively strong, but they disappear on evacuation at 400°C. In their studies of pyridine on NaX, Ward (*9*) and Nishizawa *et al.* (*10*) concluded from the infrared spectra of adsorbed pyridine after evacuation at 250°C that dehydrated NaX had the species bonded by weak coordination with sodium ions, but that no Brønsted acid sites existed. It is suggested that the adsorbed species absorbing at 260 nm corresponds to those in the infrared spectra, and are due to pyridine coordinated with sodium ion on NaX. The species which showed the bands with vibrational structure at 256 nm remained after the evacuation at 400°C. The bands are quite similar to those of hydrogen bonded or protonated pyridine. The species should be assigned to protonated pyridine, because they are more stable than pyridine coordinated with sodium ion on NaX, and the pore size of NaX is not so small (10 Å) that the hydrogen bonded pyridine in the pore would be easily removed by evacuation.

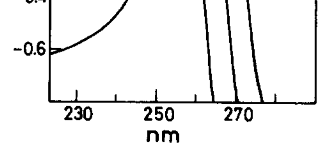

FIG. 4. Reflectance spectra of pyridine adsorbed on NaX. (a) After evacuation at room temperature; (b) after evacuation at 250°C; (c) after evacuation at 400°C.

Watanabe and Habgood (*11*) found that NaX has Brønsted acid sites under the conditions of partial dehydration at 150 ~ 200°C, but no Brønsted acid sites under condition of complete dehydration. The samples of Ward (*9*), Nishizawa *et al.* (*10*), and ourselves are under the condition of complete dehydration at 400 ~ 480°C. However, Ward, and Nishizawa *et al.* have not detected Brønsted acid sites on NaX. This result is inconsistent with our result. The main reason for this discrepancy seems to be the difference in the magnitude of extinction coefficient. The extinction coefficient of the π–π^* transition in the ultraviolet region is usually greater ($\epsilon \eqsim n \times 10^4$) than that of the infrared absorption ($\epsilon \eqsim n \times 10^2$), and that of the infrared band (1545 cm^{-1}) indicative of Brønsted acid sites is especially small. Hence, it is difficult to detect a small amount of Brønsted acid sites from infrared spectra, but this can be achieved in ultraviolet spectra. Ward (*12*) also reported that Brønsted acid sites on NaY zeolite could not be observed from the infrared spectra of adsorbed pyridine. Lombardo *et al.* (*13*) reported that the catalytic activity of NaY zeolite for 1-butene isomerization was associated with a small amount of impurities or decationated sites which generated Brønsted acid sites. Pure NaY with no cation deficiency and no divalent cations would have negligible catalytic activity. This result indicates the existence of a small amount of Brønsted acid sites on NaY which cannot be detected from the infrared spectra. The Brønsted acid sites of our sample are probably generated by a small amount of impurities or decationated sites.

In conclusion, the π–π^* band of pyridine adsorbed on acidic solids showed the peak maximum shifted to longer wavelengths from that of pyridine vapor. The bands of protonated pyridine or those of hydrogen bonded pyridine showed characteristic vibrational structure with a peak maximum at 256 nm. The pyridine coordinated with Lewis acid sites showed a broad band shifted to longer wavelength than that of protonated pyridine. In this case, the shift of the π–π^* band is considered to be determined by the degree of π-interaction between the π-conjugation system of nitrogen and an adsorbent metal ion. The ultraviolet spectra study has an advantage in the detection of a small amount of adsorbed pyridine due to the large extinction coefficient of the π–π^* band, though it is very difficult to distinguish the various types of acid sites present on the surface because of the similarity of the positions of the respective peak maxima.

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