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Reduction of Fluorescence from High-Area Oxides of the Silica, γ-Alumina, Silica–Alumina, and Y-Zeolite Types and Raman Spectra for a Series of Molecules Adsorbed on These Surfaces

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It is shown that strong fluorescence that occurs with untreated high-area samples of porous silica-glass, silica gel, Cab-O-Sil, γ-aluminas, a silica-alumina and sodium Y zeolite is in all cases eliminated or greatly reduced by heating in oxygen for several hours at 500°C. This fluorescence is attributed to traces of hydrocarbons decomposed on the acidic oxide surfaces that burn away in oxygen. Some degree of fluorescence returns when alumina-containing oxides are heated at elevated temperatures in a normal high vacuum; this is attributed to slow migration of hydrocarbon impurities. Certain organic molecules, such as furan and acetone, also give rise to new fluorescence, through decomposition, on contact with porous glass surfaces or while a Raman spectrum is being obtained. After heating in oxygen at 500°C the aluminas or alumina-containing oxides exhibit a residual weaker fluorescence between 13,000 and 14,600 cm^{-1}, which may be attributed to traces of Fe^{3+} impurities.

Raman scattering has been observed for all of the main bands active in pyridine, and variations in position, half-height width and relative intensity were observed. The bands in the 3000 and 1000 cm^{-1} regions from pyridine on the several forms of silica, when considered in relation to parallel infra-red studies, can be interpreted in terms of an initially adsorbed species involving a strong hydrogen bond between surface OH groups and the pyridine nitrogen lone-pair. Physically adsorbed pyridine, with a spectrum similar to that of the pure liquid, occurs at higher coverage. Three species are observed from pyridine on BDH γ-alumina, two of them similar to those found on silica, and the third probably held to the surface by a coordinate linkage involving the nitrogen atom. Pyridine adsorbed on NaY zeolite appears to be held to the cationic sites.

Raman spectra have been obtained by adsorption of a number of other molecules on porous glass, including benzene, methyl iodide, and several substituted benzenes. In the early stages of adsorption benzene and aniline gave spectra notably different from those of the pure liquids, and possibly attributable to species held to the surface through hydrogen-bonding involving surface OH groups.

INTRODUCTION

Infrared spectroscopy is very widely used in surface chemical studies (*1*, *2*) but is limited by the fact that certain adsorbents absorb radiation strongly over considerable ranges of the spectrum. This is true, for example, of the important classes of catalysts based on silica and alumina (and for metals supported on these oxides), which strongly absorb radiation in several frequency ranges below 1300 cm^{-1}. Although a great deal of valuable information has been obtained by infrared means in such cases (*1*, *2*) the interpretations of the spectra of the adsorbed species have to depend on the bands not obscured by these strong absorptions of the adsorbent. Since these oxide-based catalysts have only weak Raman vibrational bands,

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(*3*) the latter method is potentially a very attractive one for obtaining additional vibrational frequencies from adsorbed species in such cases, although allowance has to be made for the fact that Raman spectra in general are often much weaker than infrared spectra.

Early attempts were made to obtain Raman spectra of adsorbed species using mercury lamps as the source of powerful monochromatic radiation by Karagounis and Issa (*4*) and Pershina and Raskin (*5*). Considerably more progress has been made since the intense and highly collimated beams from lasers have become available as Raman sources (*3*, *6–8*). However, several substantial problems remain to be overcome if Raman spectroscopy is to be applied widely and routinely to problems in surface chemistry. A particularly important and common difficulty has been the strong general emission, usually assumed to be fluorescence, that occurs when the monochromatic laser beam impinges on the adsorbent itself (*3*, *7*). Typically, this fluorescence has a smooth and broad-banded spectrum, with a half-width of about 2000 cm^{-1}, with a maximum between 400 and 1600 cm^{-1} on the Stokes side of the exciting line. Its intensity is 1–3 orders of magnitude greater than the Raman spectrum of an adsorbed species so that the latter is very difficult to observe because of noise fluctuations arising from the fluorescent background. Hendra and Loader (*3*) have shown that the intensity of this background emission may often be reduced to an acceptable level in relation to Raman lines by preirradiating a fixed part of the sample with the laser beam for a number of hours before attempting to record the spectrum. However, the method is usually only partially successful, and clearly is very inefficient from the point of view of use of the Raman spectrometer.

The work described here falls into three parts. First, we report studies of the fluorescence from porous silica-glass—an adsorbent that has previously been characterized extensively by infrared spectroscopic and other methods—as a function of a variety of pretreatments. As has previously been reported briefly (*6*), this study has led to a procedure that eliminates the fluorescent background. We also report here its application to a range of other adsorbents of the silica, silica-alumina, and alumina types and find it to be to some degree effective in all cases. However, we find that a secondary residual fluorescence often remains with the alumina-containing adsorbents, including the zeolite. Secondly, this paper is concerned with the study of Raman spectra from pyridine adsorbed on a range of these adsorbents and, third, with a study of the Raman spectra from a wider range of adsorbates on porous silica-glass.

Experimental

Materials

The porous glass (150–200 $m^2 g^{-1}$) used in this work contained 96% silica, the remaining 4% being principally Al_2O_3 and B_2O_3 according to its manufacturer, the Corning Corporation (*9*). Two other forms of silica were studied, Cab-O-Sil H5 having 270 $m^2 g^{-1}$, a silica prepared by flame hydrolysis of $SiCl_4$ supplied by the Cabot Corporation, and a silica gel (BDH chromatographic grade, Cat. No. 15049). Three aluminas were studied, γ-alumina (BDH Cat. No. 15001), a γ-alumina manufactured by Degussa, and Alon C, a microspheroidal alumina formed by flame hydrolysis and manufactured by the Cabot Corporation. In addition, NaY zeolite (Union Carbide Corporation, Linde Molecular Sieve Division) and a commercial silica-alumina cracking catalyst (Ketjen N.V. code LA-3P) were examined.

For the Raman experiments, the porous glass samples were 25 × 5-mm discs, weighing about 3 g, cut from 50 × 50 × 6-mm plates. The silica-alumina was examined as supplied, in the form of 1-mm diameter pellets. All other adsorbents were studied in the form of pressed discs.

Infrared transmission spectra were obtained from thin plates of porous glass (0.5 × 25 × 10 mm), and from pressed discs of Cab-O-Sil.

Most adsorbates studied were BDH Analar grade chemicals and were used as supplied (acetone, furan, dioxan, methyl iodide) or after redistillation (pyridine, benzene, benzyl alcohol, benzyl chloride, chlorobenzene). A few adsorbates were redistilled reagent grade BDH chemicals (aniline and benzylamine). In all cases the adsorbate liquids were degassed by repeated freeze-pump-thaw cycles. Solutions containing 10% (volume/volume) of pyridine were prepared in distilled H_2O, 1 *M* HCl, and BDH Analar CH_3COOH, CH_3OH, CH_3COCH_3 and CCl_4. Other adsorbates investigated were Air Products Co. 98% N_2O, National Physical Laboratory research grade C_2H_2 and British Oxygen Company X-grade CO_2.

Apparatus

Raman spectra were obtained with a Spex Industries laser-Raman spectrophotometer using a Spectra-Physics Model 125 He–Ne laser, 90° illumination-collection optics and a Model 1401 double monochromator. The main neon lasing line at 15,802 cm^{-1} was employed, yielding 40–60 mW without r.f. stabilization of the plasma. Sample discs were held at an angle of incidence of 60° with respect to the laser beam, which was focused inside or in front of the disc. The focal point of the incident beam was generally inside the scattering disc to avoid localized heating, which was often followed by an increase in the background fluorescence when some adsorbates were present. An angle of incidence of 60° was chosen to avoid direct reflection of the beam into the monochromator and, hence, to narrow the effective width of the scattered exciting line. Scattered radiation was centered and focused so as to fill the entrance slit of the monochromator. Such radiation was dispersed by a grating of 1200 lines/mm, blazed at 5000 A and with a principal grating ghost at $\Delta\nu = 2906$ cm^{-1}. Signals were detected by a type FW 130 shielded photomultiplier, operated at room temperature, and were amplified by linear photon-counting. As is generally the case for helium–neon laser excitation, the reduced sensitivity of this photomultiplier at lower wavenumber leads to reduced observed intensities for the Raman lines with high values of $\Delta\nu$, particularly above $\Delta\nu = 3000$ cm^{-1}.

Raman spectra were recorded in most cases with slit widths of 600 μm which gave a resolution of 8.0 cm^{-1} at 15,802 cm^{-1}. The same resolution was used to record spectra of the same substance in the liquid, solution and adsorbed states. Instrument calibration was checked over the range $\Delta\nu = 100$ to 3000 cm^{-1} using non-lasing lines and carbon tetrachloride; frequencies are accurate to ± 1 cm^{-1} for sharper lines.

Infrared spectra of adsorbates on porous glass were recorded on a Perkin-Elmer Model 621 double-beam spectrophotometer. Spectra below 2000 cm^{-1} were obtained only with considerable reference-beam compensation and the use of five-times ordinate expansion. Infrared spectra of adsorbates on Cab-O-Sil discs were obtained on a Grubb-Parsons GS2 double-beam grating spectrophotometer.

A typical cell for the Raman experiment, Fig. 1, consisted of a quartz tube, for sample treatment, joined to a pyrex tube and sample window. This type of cell was used either with greased joints and taps, or as a sealed tube with a Teflon greaseless tap. In the latter case, a liquid-nitrogen trap

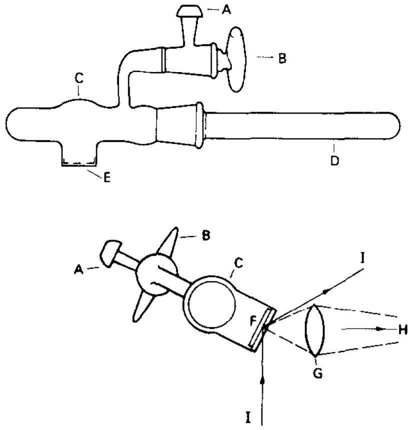

FIG. 1. Horizontal and vertical cross-sections of the cell used to obtain Raman spectra of oxide samples in disc form. (A) Ball-joint connecting cell to vacuum-line; (B) vacuum tap; (C) body of the cell; (D) quartz section of the cell for heating the oxide disc; (E) optical window; (F) disc-shaped sample; (G) collecting lens for Raman radiation; (H) spectrometer; and (I) laser beam.

protected the cell and sample from contaminants.

Raman cells were mounted reproducibly on the sample compartment housing with an adjustable holder. The latter was mounted on an optical rail and allowed the cell to be adjusted parallel to the laser beam, parallel to the spectrometer optic axis, and perpendicular to the plane containing the optic axis and the laser beam. Furthermore, the angle of the sample plane with respect to the laser beam could be varied. The whole of this assembly was covered with a black cloth to eliminate stray radiation.

The infrared spectra of porous glass were obtained with a cell similar to that described by Kozirovski and Folman (*10*).

Procedures

The pretreatment of the porous glass discs has been described previously (*6*). The samples were placed in a quartz tube, whose temperature could be measured with a chromel-alumel thermocouple, and were then heated slowly to 500°C and kept at this temperature for 12–15 hrs in a stream of oxygen. The samples were then evacuated in a complete Raman cell. Similar procedures were used for the other samples. For porous-glass, the evacuation temperature was varied between 250 and 750°C. The evacuation temperatures were 330°C for Cab-O-Sil, silica-gel, and NaY zeolite, and 230°C for alumina or silica-alumina. When the latter group of adsorbents was evacuated at high temperature after oxygen pretreatment, the fluorescence increased again. Experiments with NaY zeolite showed that this increase in fluorescence during evacuation at 350°C occurred even when the zeolite was evacuated in a greaseless cell and protected from grease and mercury vapor by a liquid nitrogen trap.

The Raman cell was mounted on the spectrometer and connected to a conventional all-glass vacuum system. Glass joints and taps on the vacuum line were greased with Apiezon N, those on the cell were greased with Apiezon T, and those on the adsorbate bulb with Silicone grease. Adsorbates were initially added in a controlled manner via the gas phase, and spectra were scanned until equilibrium was attained during adsorption. During the initial stages of adsorption of low vapor-pressure liquids, and in all cases during the later stages of adsorption, discs were exposed to the equilibrium vapor pressure of the adsorbate at room temperature.

Typically, Raman spectra were recorded over the range $\Delta\nu = -1500$ cm^{-1} to $+3200$ cm^{-1} for the untreated disc, the disc after heating in O_2, after heating in vacuum, and during successive stages of adsorption and desorption. Normal settings used to record spectra of the 1000 cm^{-1} region for pyridine adsorbed on porous glass were: 500 counts per second for a full-scale recorder deflection, a time-constant of 10 s, zero suppression between 0 and 10, all three slits at 600 μ with full height, a scan speed of 5 cm^{-1} min^{-1} and a 20-in. hr^{-1} chart speed.

RESULTS

Laser-Induced Fluorescence Spectra of Adsorbents

Laser-induced radiation from four groups of solids was studied. The groups were: (1) several forms of silica; (2) several samples of aluminas; (3) a silica-alumina; and (4) NaY zeolite, a crystalline aluminosilicate.

The laser-induced fluorescence spectra of untreated samples of the three forms of silica investigated are compared in Fig. 2 A, B, and C. By untreated we mean adsorbent samples that had been in contact with air during storage or preparation. The figure-caption provides information about the different relative sensitivities used, which vary considerably from case to case. Porous glass gave a very broad fluorescence band with a maximum centred near $\Delta\nu = 400$ cm^{-1} and a shoulder near 1700 cm^{-1}. Silica gel showed a considerable weaker fluorescence with a maximum at *ca.* 500 cm^{-1} and another maximum of similar intensity centred near 1400 cm^{-1}. Cab-O-Sil showed considerably weaker fluorescence overall with a single maximum between $\Delta\nu = 300$ and 400 cm^{-1}. In all those cases, the adsorbent SiO_2 Raman band near 460 cm^{-1} could be seen.

Although these three adsorbents in untreated form gave rather different fluo-

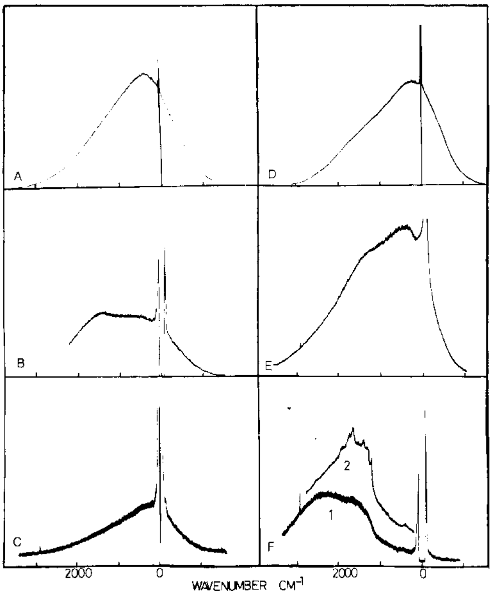

FIG. 2. Fluorescence background spectra for several oxide samples; the numbers in brackets listed below denote the number of counts per second for full scale of the recorder and are inversely proportional to the amplification. (A) Untreated porous glass (10^5); (B) untreated silica-gel (2×10^4); (C) untreated Cab-O-Sil (10^4); (D) porous-glass after exposure to furan (10^5); and (E) untreated BDH γ-alumina (2×10^4) (F1) BDH γ-alumina (10^4) and (F2) Degussa γ-alumina (10^5), both after heating in O_2 at 500$_o$C.

The single or double sharp lines or double peaks in the vicinity of $\Delta\nu = 0$ cm^{-1} arise from the laser exciting line as modified by automatic or manual beam cut-off.

rescence spectra, they were all affected in the same way by heating and/or evacuation. It was not possible to depress appreciably the laser-induced spectra by simply heating such samples to 500°C in vacuum; indeed such heating of untreated samples caused an increase of fluorescence. However, heating the samples in a stream of oxygen at 500°C for 10–12 hr led to a *virtual elimination* of the intense fluorescence bands in all three cases. Subsequent evacuation did not cause the laser-induced spectrum to reappear, even when the evacuation temperature was as high as 800°C.

During later adsorption studies, it became apparent that certain adsorbates themselves caused an increase in the laser-induced radiation from porous-glass. A particularly large effect followed the exposure of a porous-glass disc, previously heated in O_2 at 500°C and then outgassed at 500°C, to furan vapor at 20°C. The disc became visibly tinted in 20–30 sec and was a deep orange-brown color in 10–15 min. This apparent decomposition of the furan was accompanied by the growth of intense fluorescence features, not dissimilar in outline to those obtained with untreated porous glass, with a main maximum near $\Delta\nu = 200$ cm^{-1} and a shoulder at *ca.* 1500 cm^{-1} (Fig. 2D). Less marked effects of this type followed exposure of the porous-glass disc to acetone, dioxan, and benzene.

The laser-induced fluorescence spectra of BDH γ-alumina, measured before and after the heat treatment in O_2 at 500°C, are shown in Figs. 2E and 2F. In contrast to the silica adsorbents, in the γ-alumina case the O_2 treatment does not fully remove all of the fluorescence.

In this case, the untreated material (Fig. 2E) showed a main maximum centred between $\Delta\nu = 400$ and 500 cm^{-1}, a substantial shoulder near 1200 cm^{-1} and a broad tail extending to higher frequencies. After heating the same sample in O_2 at 500°C, much of the fluorescence was removed but a residual feature was uncovered that was centred near $\Delta\nu = 2000$ cm^{-1} i.e., $\nu \sim 13{,}800$ cm^{-1}, with a half-width of about 1600 cm^{-1} (Fig. 2F1). For the Degussa γ-alumina (and also Alon C), treatment in O_2 for 16 hr at 500°C again led to the removal of the main fluorescence, but left a residual band (Fig. 2F2), which appears to consist of a broad component similar to that for BDH γ-alumina with an additional structured component with the strongest peak at $\Delta\nu = 1580$ cm^{-1}. Similar residual fluorescence phenomena to those shown in Figs. 2F1 and 2F2 were obtained from the silica-alumina catalyst and the sodium Y zeolite after O_2 treatment at 500°C.

Unlike the silicas, all these alumina-containing materials showed growth of fluorescence once again during pumping at elevated temperatures after O_2 treatment. Thus, BDH γ-alumina held at a temperature of 230°C for 16 hr showed an increase of the

TABLE 1

POSITIONS ($\Delta\nu$ CM^{-1}), HALF-WIDTHS ($\delta\nu_{1/2}$ CM^{-1}) AND RELATIVE PEAK INTENSITIES (I) OF RAMAN LINES OF PYRIDINE IN THE LIQUID STATE AND ADSORBED ON HIGH-AREA SILICA SAMPLES

Liquid pyridine			Adsorbed on porous glass (275°C)			Adsorbed on porous glass (475°C)			Adsorbed on porous glass (770°C)			Adsorbed on silica gel		Adsorbed on Cab-O-Sil	
$\Delta\nu$	$\delta\nu_{1/2}$	I.	$\Delta\nu$	$\delta\nu_{1/2}$	I.	$\Delta\nu$	$\delta\nu_{1/2}$	I.	$\Delta\nu$	$\delta\nu_{1/2}$	I.	$\Delta\nu$	I.	$\Delta\nu$	I.
									l 3099	11	8				
			l 3075	16	6	*l* 3075	13	7	*l* 3073	13	20				
3089	wsh		*h* 3070	14	—	*h* 3070	sh	—	*h* 3070	10	3	*h* 3070	sh	abs	
						l 3070	9	7	*l* 3066	13	15				
3058	23	14	*h* 3059	14	14	*h* 3059	25	15	*h* 3057	14	10	*h* 3061	19	*h* 3063	15
						l 1597	~15	9							
			h 1596	10	7	*h* 1597	16	5	*h* 1598	10	2	*h* 1600	4		
						l 1580	~10	7							
1584	30	8	*h* 1578	17	7	*h* 1577	18	7	*h* 1578	20	4	*h* 1578	6		
			h 1231		wsh	*h* 1232		wsh	*h* 1231		wsh				
						l 1220	15	12							
1220	18	7	*h* 1217	13	14	*h* 1217	15	8	*h* 1219	14	7	*h* 1219	9		
			l 1037	7	50	*l* 1035	10	41	*l* 1035	11	68	*l* 1035	100	*l* 1037	60
1030	8	78	*h* 1034	10	98	*h* 1032	9	87	*h* 1030	6	71	*h* 1032	87	*h* 1033	92
			l 1007	12	100	*l* 1007	13	100	*l* 1007	15	100	*l* 1006	45	*l* 1009	100
			h 1009	15	85	*h* 1007	13	54	*h* 1006	10	9	*h* 1008	60	*h* 1007	53
			l 993	sh	12	*l* 993		sh	*l* 993	10	47				
991	7	100	*h* 993	9	100	*h* 993	8	100	*h* 991	6	100	*h* 991	100	*h* 992	100
						l 655	8	10	*l* 653	8	20				
656	15	15	*h* 653	10	13	*h* 652	12	12	*h* 655	6	7	*h* 655	11		
						l 618		10							
			h 616	20	7	*h* 618	15	6	*h* 620	sh	2	*h* 617	3		
						l 606		7	*l* 609	28	15				
605	18	6	*h* 605	15	9	*h* 606	16	7	*h* 606	6	4	*h* 605	3		

Abbreviations: wsh, weak shoulder; abs, absent; I., relative intensity, peak height; *l*, low coverage; *h*, high coverage.
Not all regions were scanned in the early stages, but other regions seem insensitive to coverage.

main fluorescence features by five times at 2000 cm^{-1} (possibly caused by overlap of the main band) and 20 times in the 450 cm^{-1} region. However, the regenerated intensity was considerably less than that from the untreated alumina.

In contrast, when the silica-alumina catalyst (Ketjen LA-3P) was evacuated for 4 hr at 500°C, a 100-fold increase in intensity at 400 cm^{-1} occurred over that previously observed for the same sample after 16 hr O_2 treatment at 500°C. For the crystalline alumino-silicate, NaY zeolite, subsequent evacuation (even in a greaseless cell with the full precautions described under experimental procedures) at higher temperatures, up to 530°C, led to a steady increase in the fluorescence feature centred near 400 cm^{-1}. For example, after 1 hr evacuation at 500°C this feature was as intense as for the starting material. However, evacuation for 1 hr at less than 330°C gave a sufficiently weak background fluorescence spectrum that it was possible to detect adsorbate Raman bands above the noise level.

Raman Spectra of Adsorbed Pyridine

Pyridine Adsorption on Porous Silica-Glass, Silica Gel, and Cab-O-Sil

The observed Raman frequencies resulting from the adsorption of pyridine on the several forms of silica are given in Table 1. In the text we shall concentrate on the structurally more significant bands in the $\Delta\nu = 3000$ and 1000 cm^{-1} regions. Our results in the latter region are similar to those reported by Hendra, Horder, and Loader (*3*) for pyridine on silica-gel and on Cab-O-Sil, but we have also studied several samples of porous glass, and have recorded results over a wider range of frequencies.

Figure 3 shows a low-coverage Raman spectrum for pyridine on a porous silica glass disc after exposure to multiple doses of vapor from liquid pyridine followed by desorption by pumping for 11 hr at 20°C. In this case, the porous glass had been oxygen pretreated at 500°C and outgassed at 475°C. During adsorption on this sample, the first detectable Raman lines were similar to those shown in Fig. 3 and occurred at 3078(6)-3070(7) and 1035(41), 1007(100) and 993(sh) cm^{-1}, where the numbers in brackets denote relative peak heights of the bands within a given spectrum [strongest intensity = 100], and (sh) stands for shoulder. On continued adsorption, the bands at 3078, 1035, and 1007 cm^{-1} soon reached maxima in their intensity and were overtaken by neighboring bands that appear at higher coverage as shown in Figs. 4, 5, and 6 for similar samples. At the same time, the bands at 3078 and 1035 cm^{-1} themselves move

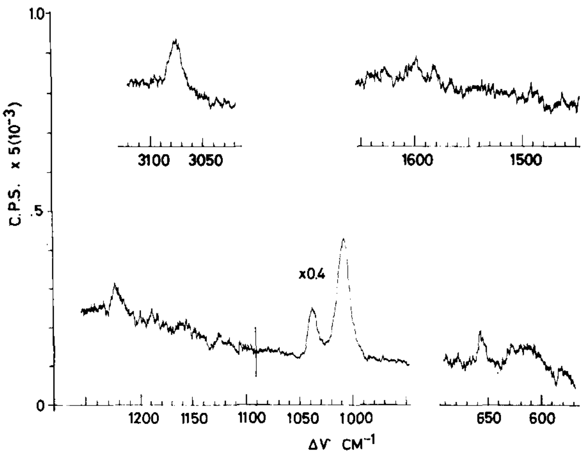

FIG. 3. The Raman spectrum of pyridine adsorbed on a porous silica-glass disc, which had been pretreated at 500°C in oxygen and at 475°C in vacuum. The bands were observed after pumping for 11 hrs at 20°C on a highly exposed sample. C.P.S., counts per second.

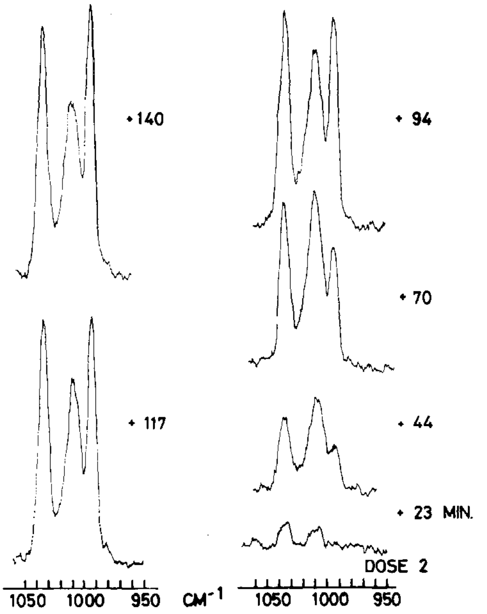

FIG. 4. The growth of the Raman bands in the 1000 cm^{-1} region as a function of time for the second dose of pyridine adsorbed on a porous-glass disc, previously treated at 500°C in oxygen and at 675°C in vacuum. No bands had been observed for the first dose.

toward 3070 and 1032 cm^{-1}, respectively. At the higher coverages, these two regions of the spectrum for the same sample outgassed at 475°C show bands at 3070(sh), 3059(15) and 1032(87), 1007(54), and 993(100) cm^{-1}. As will be discussed below, the additional bands are probably due to physically adsorbed pyridine, as they are similar to those obtained with liquid pyridine, whereas the initial spectrum must be caused by molecules that are strongly perturbed. The bands of the lightly perturbed molecules were readily decreased in intensity again when pyridine was desorbed by pumping at room temperature. After desorbing from the highly pyridine-covered porous-glass by pumping for 11 hr at 20°C, residual bands were found at 3072(15), 1036(38), and 1008(100) cm^{-1}, similar to those observed in the early stages of adsorption. They too could be decreased in intensity if the disc was pumped at a higher temperature, i.e., 100°C.

Similar spectra were observed when pyridine was adsorbed on porous glass discs pretreated in oxygen at 500°C and then outgassed at either 275, 675, or 770°C. In each case, the appearance of the initial strongly perturbed bands was followed by the development of weakly perturbed bands at higher coverage. It had been hoped that it might have been possible to measure differences between the relative intensities of the weakly and strongly perturbed bands as a function of the outgassing temperature, *i.e.*, as a function of the surface hydroxyl group concentration. Although no firm evidence of a temperature dependence could be found, we believe this is mainly due to our inability to control and detect equal small doses of pyridine among the various samples.

Raman spectra were not always observed for the initial doses of pyridine on porous glass, even though the doses were apparently rapidly adsorbed. Thus, in one experiment Raman bands were not observed during the adsorption of the first three doses of pyridine vapor. The adsorption of the fourth dose led to the appearance of a Raman band near 1008 cm^{-1} of such an intensity that bands with a quarter of this intensity (i.e., a spectrum such as might be expected from the first dose) should not have escaped notice. To ensure that the initial doses of pyridine were not being adsorbed near the outer layers of the disc, i.e., outside the section of the disc irradiated by the laser beam, repeated attempts were made to observe a Raman signal near 1000 cm^{-1} by refocusing the beam at various positions on the disc, i.e., across the face of the disc from the edge to edge. In addition, doses were adsorbed with the incident laser beam focused on and off the sample, but the results were the same, i.e., no spectrum was observed. No increase in the general level of background radiation was noted during these doses, so there is no evidence that the pyridine was decomposing. These difficulties were not encountered with the other oxides, but in general the porous glass discs were approximately twice as thick as the others.

Typically the first spectra of adsorbed species were observed when about one or two doses (a dose consisting of 3.3 × 10^{-3} cm^3 of pyridine vapor reduced to STP) had been

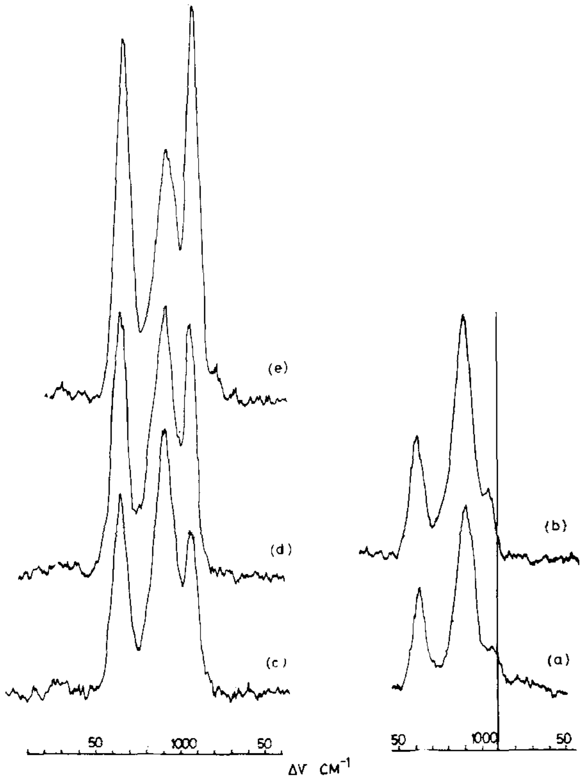

FIG. 5. The growth of the bands in the 1000 cm^{-1} region for the Raman spectrum of pyridine adsorbed on a porous-glass disc outgassed at 275°C: (a) dose 1; (b) dose 2; (c) dose 3, (d) dose 4; and (e) dose 7. These spectra were all recorded after equilibrium had been attained. Note that it has taken seven doses to reach the same spectral state as two doses achieved in Fig. 4.

adsorbed on a porous-glass disc weighing about 3 g.

At high coverages, when the first bands had ceased to grow and the second set of bands were well developed, the appearance of the disc changed from almost transparent to an opaque milky white. The sample became clear again at very high coverages. This behavior is well known (*11*) and corresponds to the range of pressures associated with the hysteresis loop of the adsorption isotherm. Without measurements of the resulting changes in the light-scattering properties of the disc it is impossible to relate accurately the observed intensity of the Raman bands to the pyridine content of the glass. Conversely, during the desorption of pyridine it was often possible to see a transparent envelope along the edges of the porous glass, while the center was still milky. The central milky zone persisted after the disc had been left to equilibrate for several hours, indicating slow mobility of the adsorbed pyridine. There were no additional changes in the spectrum accompanying this opacity.

Parallel infrared studies on porous-glass showed that the adsorption of pyridine at similar vapor pressures was accompanied by a slight decrease in the intensity of the νOH stretching band at ca. 3690 cm^{-1} due to "free" OH groups on the silica surface, together with the growth of a broad band centred near 2910 ± 20 cm^{-1}, with a half-height width (on the absorbance scale) of about 1040 cm^{-1}, caused by surface OH groups that are strongly hydrogen-bonded, presumably to the nitrogen lone-pair on pyridine. At the same time, infrared bands due to adsorbed pyridine developed at 3085,

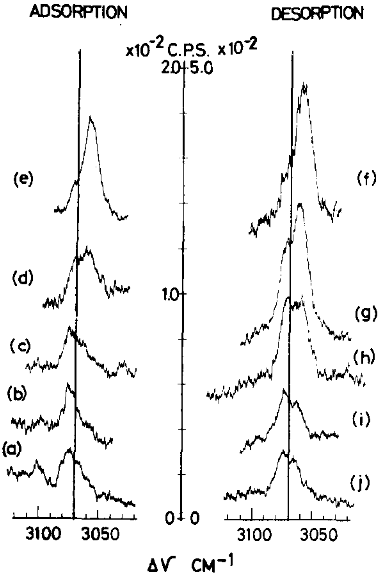

FIG. 6. Changes in the νC–H stretching bands in the Raman spectrum of pyridine adsorbed on a porous-glass disc, which had been outgassed at 770°C. Spectra (a–e) are for doses 2–6 in the adsorption and spectra (f–j) for various consecutive stages of the desorption by pumping at 20°C. C.P.S., counts per second.

3050, and 1594 cm^{-1}, the region below 1400 cm^{-1} not being available for study because of a black-out resulting from absorption of radiation by the adsorbent. Pumping overnight at room temperature decreased the intensity of the pyridine bands and caused the maxima of the broad hydrogen-bonded νOH band at 2910 cm^{-1} and the pyridine band at 1594 cm^{-1} to shift to about 2850 and 1605 cm^{-1}, respectively.

Table 1 shows that the adsorption of pyridine by silica-gel and Cab-O-Sil gave rise to Raman spectra similar to those observed for the adsorption of pyridine on porous-glass. The infrared spectrum of pyridine on Cab-O-Sil was observed to have bands at 3755 ("free" νOH), 3705 (sh, νOH) and 2906 (broad, hydrogen-bonded νOH) and at 3100, 3072, 3050, 1605, and 1453 cm^{-1} for low and intermediate coverages of pyridine. At higher coverages the "free" νOH band continued to decrease in intensity while the νOH band shifted to *ca.* 3690 cm^{-1}. The other bands remained much the same except for the reproducible appearance of a shoulder at 1583 cm^{-1} and the appearance of a band at 1487 cm^{-1} correlated with very large doses of pyridine, as indicated by the absence of a "free" νOH band.

Pyridine Adsorption on γ-Alumina and NaY-Zeolite

After BDH γ-alumina (heated at 500°C in oxygen and evacuated at 330°C) had been continuously exposed to pyridine vapor over the liquid for 5.5 min, Raman bands were observed at 3056(16), 1032(93), 1018(45), 1000(sh), 992(100), 654(15), and 608(5) cm^{-1}. The 1050 to 950 cm^{-1} spectral region is shown in Fig. 7. Desorption caused major changes in the relative intensities of the bands in the 1000 cm^{-1} region (Fig. 7, a,

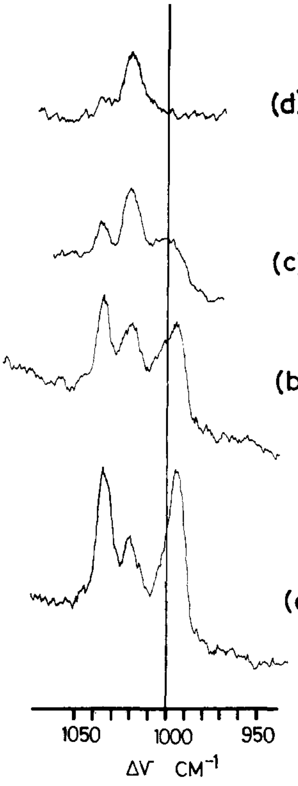

FIG. 7. Changes in the 1000 cm^{-1} region of the Raman spectrum of pyridine adsorbed on BDH γ-alumina during desorption: (a) P = 12.5 Torr; (b) P = 3.5 Torr; (c) sample pumped for 30 sec and equilibrated for 40 min; and (d) sample pumped for a total of 57.5 min in five stages, and equilibrated for 33 min.

b, c, and d). The two strongest bands present after exposing the sample to 12 Torr of pyridine vapor at 992 and 1032 cm^{-1} were both rapidly reduced in intensity on pumping. All the former, and much of latter had disappeared after 20 min pumping. Removal of the 992 cm^{-1} band revealed another at 1000 cm^{-1}, discernible only as a shoulder in the original spectrum, which was then pumped away in turn before the band at 1018 cm^{-1} had been much reduced. We conclude that the Raman spectroscopic evidence reveals three different surface species characterized by the frequencies (1) 992 and 1032 cm^{-1}, (2) 1000 cm^{-1} and perhaps a contribution at 1035 cm^{-1} to the 1032 cm^{-1} absorption, and (3) 1018 (strong) and 1032 cm^{-1} (weak), in the order of increasing strength of adsorption. With the exception of our finding a weak companion band at 1032 cm^{-1} to that at 1018 cm^{-1}, these results are very similar to those obtained previously by Hendra, Horder, and Loader (*3c*) for pyridine on η-alumina. The latter authors also studied pyridine on a γ-alumina but obtained more complex spectra than ours.

Adsorption of pyridine on NaY zeolite gave a Raman spectrum with bands at the somewhat different frequencies of 3070(11), 1596(8), 1218(15), 1036(61), 1002(100), 654 (20), and 613(7) cm^{-1}. The NaY sample had been heated 18 hr at 500°C in O_2 and 18 hr in vacuum at 350°C in a greaseless cell isolated from the vacuum line by a liquid-nitrogen trap attached directly to the cell. After exposure to 100 Torr oxygen at 350°C it was finally evacuated for 1 hr at that temperature.

Other Molecules Adsorbed on Porous Glass

The spectrum of adsorbed benzene was recorded as a function of coverage and bands were observed at 3064(12), 3048(7), 1607(7), 1588(9), 1179(15), 994(100), 983(13), 943 (15), 916(13), 858(20), 828(10), and 608(23) cm^{-1}. With the exception of the bands at 828 and 858 cm^{-1} all of these bands are found in the spectrum of liquid benzene. However, as is shown in Table 2, the relative intensities of some of these bands differed appreciably from those of the liquid spectrum, and this effect was in general most noticeable at low coverages. In our earlier communication (*6*), we reported some marked changes in the relative intensities of the 3048 and 3064 cm^{-1} bands. Further work has shown that the enhanced intensity of the 3048 cm^{-1} band relative to the band at 3064 cm^{-1} does not occur during the first stages of adsorption, but develops at an intermediate coverage as shown in Table 2. Continued adsorption results in the relative intensity of the 3048 cm^{-1} band decreasing to its normal value once more. Also, the enhanced intensity was not observed during the desorption of the benzene, i.e., it was an irreversible phenomenon.

TABLE 2
THE EFFECT OF INCREASING DOSAGE UPON THE RELATIVE INTENSITIES OF THE MORE PROMINENT BANDS IN THE RAMAN SPECTRUM OF BENZENE ADSORBED ON POROUS SILICA-GLASS

Band position	Dose 1	Dose 3	Dose 4	Dose 4 after 10 days equilibration	Liquid
cm^{-1}					
608	23	19	13	3	7
994	100	100	100	100	100
1179	15	17	16	14	6
1588	9	9	ns	4	3
1607	7	ab[a]	ns[b]	ab	3
3048	7	11	11	2	3
3064	12	11	15	10	12

[a] Absent or very weak.

[b] Not scanned.

TABLE 3

THE POSITIONS ($\Delta\nu$ CM^{-1}) AND RELATIVE INTENSITIES (I) OF THE RAMAN BANDS OF SOME SUBSTANCES ADSORBED ON POROUS-GLASS COMPARED WITH THE SAME SUBSTANCES IN LIQUID STATES

Aniline				Benzylamine				Chlorobenzene				Dioxan			
Adsorbed		Liquid		Adsorbed		Liquid		Adsorbed		Liquid		Adsorbed		Liquid	
$\Delta\nu$	I.	$\Delta\nu$	I.	$\Delta\nu$	I.	$\Delta\nu$	I.	$\Delta\nu$	I.	$\Delta\nu$	I.	$\Delta\nu$	I.	$\Delta\nu$	I.
3061	15	3055	13	3063	16	3060	sh	3069	12	3070	13	2968	34	2969	17
						3052	8					2896	19	2891	9
				1629	sh										
1606	35	1602	25	1609	13	1602	10								
				1584	8	1583	5	1584	10	1584	9	1447	19	1447	16
												1306	19	1308	18
1262	9	1279	11	1209	13	1201	10							1220	10
1182	6	1175	8	1184	6	1175	5								
1159	11	1154	10	1162	6	1157	5								
								1084	18	1084	20				
1031	61	1028	51	1032	22	1026	15	1023	35	1024	36	1017	10	1018	22
1001	100	996	100	1004	100	1003	100	1003	100	1003	100				
828	44	826	40									837	100	838	100
818	33	814	42	790	18	781	11								
				751	6	749	4								
								703	27	703	30				
620	21	619	13	622	17	620	11	617[a]	—	614	8				
				609	sh										
534	17	531	14												
		388	7					420[a]	39	419	33				
235	9	233	8					300[a]	11	298	7				
								197	28	196	31				

[a] Data less accurate.

Spectra of a range of other aromatic molecules were also recorded, and these are listed in Table 3. The spectra of adsorbed aniline and adsorbed benzylamine showed shifts in the positions of certain bands, as well as some changes in the relative intensities, compared to their liquid spectra obtained under similar resolution conditions. However, the spectra of adsorbed chlorobenzene and dioxan were very similar to their liquid phase spectra. Three bands were detected in the Raman spectrum of CH_3I adsorbed on porous glass, 2962(13), 1250(10) and 530(100) cm^{-1} at somewhat higher values of $\Delta\nu$ than found for the liquid [2950(8), 1242(6) and 524(100) cm^{-1}] and the relative intensity of the 530 cm^{-1} band has decreased by nearly 50%. Raman spectra due to acetone adsorbed on porous glass 2926(56) and 792(100) cm^{-1}, were barely distinguishable from those of the liquid [2926(49) and 789(100) cm^{-1}]. A few attempts were made to record the spectra of some weakly Raman scattering molecules in the adsorbed state, but these were not successful. For example, porous-glass adsorbs large quantities of acetylene at room temperature (*12*), but no Raman signal from an adsorbed species could be detected. Preliminary experiments with CO_2 and N_2O were similarly unsuccessful, although a more concentrated effort may yield results.

Discussion

Laser-Induced Fluorescence Spectra Arising from the Adsorbents

All four classes of adsorbents studied show the initial strong fluorescence feature centred near $\Delta\nu$ = 300–500 cm^{-1}. This is consistently removed or greatly reduced in intensity by heating in oxygen or air for a number of hours at 500°C, but sometimes returns on subsequent reheating in vacuum, particularly for aluminas or silica-aluminas. Also for the latter adsorbents there is a residual weaker fluorescence, in the range $\Delta\nu$ = 2800–1200 cm^{-1}, i.e., ν = 13,000–14,600 cm^{-1}, which persists after heating in oxygen has removed fluorescence of the first type.

A number of possible causes of these fluorescence phenomena may be envisaged such as (1) an intrinsic fluorescence originating in the bulk adsorbent, (2) an intrinsic fluorescence originating in the surface layer of the oxide adsorbents, e.g., particular active sites, (3) fluorescence originating in bulk or surface impurities associated with the oxide material, e.g., chemical impurities, crystal defects, color centres etc., and (4) fluorescence originating in non-oxide impurities probably adsorbed or trapped at the oxide surfaces (*13*).

Previous studies of massive, i.e., not finely divided, crystalline or glassy silicas or aluminas indicate that these do not give fluorescence in the red end of the visible spectrum for high purity samples. Indeed, successful Raman experiments have been carried out with bulk samples of such materials (*14*, *15*). This suggests that explanation (1) is unlikely to be the correct one for either type of fluorescence that we observed.

The main chemical impurity in the alumina-containing samples which give the residual fluorescence in the vicinity of $\Delta\nu$ = *ca.* 2000 cm^{-1} [$\nu \sim$ 14,000 cm^{-1}] is known from the analytical figures to be iron, present, for example, to the extent of 300 p.p.m. in Ketjen LA-3P silica-alumina. Being a transition metal, this seemed a likely source of fluorescence. A search of the literature showed not only that Fe^{3+} impurities are soluble in alumina (*16*), faujasites (Y zeolites), etc. (*17*, *18*), but that most of these give fluorescent or phosphorescent bands centred between 13,000 and 15,000 cm^{-1}, which are assigned to an optical transition associated with these Fe^{3+} ions in tetrahedral environments (*16–18*). Therefore, the chemical origin of the residual emission seems to be satisfactorily identified.

The efficient removal of the more intense fluorescence, centred near 15,400 cm^{-1} with helium–neon excitation ($\Delta\nu$ = 400 cm^{-1}), by heating the sample in oxygen suggests strongly that this is associated with the surface of the adsorbent, i.e., that explanations (2), (3), or (4) are appropriate. The fact that porous silica-glass exposed for a prolonged period to a laboratory environment turns yellow-brown, and that upon heating in an oven at moderate temperatures (110°C) such samples became quite dark, can be attributed to the adsorption of hydrocarbons by this highly porous material and their decomposition to unsaturated materials at higher temperature. We have always found that such tinted samples give particularly strong fluorescence (although it is also possible to obtain strong fluorescence from apparently quite clear oxide plates) and the elimination of this by heating in oxygen at 500°C is what would be expected if hydrocarbon impurities are burnt off at this temperature.*

Subsequent experiments have reinforced our view that hydrocarbon impurities, sometimes present in only very small quantities, give rise to this type of fluorescence. Thus, the adsorption of conjugated substances such as furan or benzene at room temperature gives rise to increased fluorescence of this type, presumably through decomposition of these organic compounds on the surface. In the benzene case the fluorescence decreased again on continued irradiation by the laser beam. Furthermore, silicas can be maintained in vacuum, free of fluorescence, for considerable periods at 500°C after oxygen treatment, provided care is taken to isolate the sample from sources of grease by appropriate cell design; but cells with adjacent greased joints can cause a regrowth of the fluorescence if the grease becomes even slightly warm. However, even with the better designed cells, fluorescence returns with most alumina-containing samples when retained in vacuum above about 200°C. This is presumably because these more acidic surfaces are particularly efficient at decomposing very small residual amounts of saturated hydrocarbons. These may not be completely burned out by the oxygen treatment of the sample, or may migrate from the cell walls which do not reach the same high temperature. It appears that the fluorescence provides a very sensitive indicator for the presence of hydrocarbon impurities, which in some circumstances can be very tenaciously retained by adsorbents. The decay of fluorescence in a laser-beam seems to be uniform over different parts of a given sample and to be proportionate to the intensity of the fluorescence itself.

A recent paper by Careri and others (*19*) describes experiments on the fluorescence from a range of oxides. They show that heating aluminas in vacuum to high temperatures leads to a reduction in fluorescence that is substantial above 500°C and returns when the sample is allowed to have prolonged contact with moist air. These and other experiments led them to the conclusion that strongly chemisorbed water molecules are responsible for the fluorescence. However, their experimental evidence is ambiguous, for in the case of a silica-alumina they find a marked *increase* in fluorescence on heating under vacuum (an experimental finding more in line with our experience) and the increase reported with an X zeolite could apparently also have occurred during heating in vacuo, rather than on exposure to air. At this point, therefore, we still take the view that fluorescence is very probably caused by impurities (such as hydrocarbons), which are caused to become more fluorescent when heated on an acidic oxide surface but may be partly destroyed again at very high temperatures. The increase of fluorescence reported by Careri *et al.* on prolonged contact with moist air could be caused by concomitant hydrocarbon contamination, and the reduction of fluorescence on Na-treated aluminas may well be due to the removal of acidic OH groups, which play a role in transforming saturated hydrocarbon impurities into those that give fluorescence.

We shall report later on further experiments (1) using different laser exciting lines, and (2) using mass spectrometric measurements in combination with repeated oxygen treatments of certain samples, which add further support to our interpretations of the two types of fluorescence observed. However, it cannot altogether be ruled out that explanations of type (3) as described in the second paragraph of this section play some role in the fluorescence phenomenon, which is reduced by heating in oxygen.

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* Since submitting this paper for publication we have become aware of a recent paper by E. Buechler and J. Turkevich (*J. Phys. Chem.* **76**, 2325 (1973)) in which heating in oxygen (at 600–650°C) is also recommended to reduce fluorescence that is thought to originate from hydrocarbon contamination.

Raman Spectra of Adsorbed Pyridine

Pyridine Adsorption on Porous Silica-Gel and Cab-O-Sil

The spectra and frequencies listed in Table 1 show that pyridine gives rise to the same adsorbed species on porous glass, on silica-gel and on Cab-O-Sil. In each case the initially observed species is associated with bands near 3075, 1035, and 1008 cm^{-1}. At higher coverages, the weakly perturbed bands associated with physically adsorbed pyridine are dominant. The physically adsorbed pyridine can be pumped away at room temperature, but in order to desorb the initially adsorbed species it is necessary to warm the system to 100°C. Similar results have previously been reported by Hendra, Horder, and Loader (*3*) (for Cab-O-Sil and silica-gel) and by Kagel (*7*) (for silica-gel), and the nature of the initially adsorbed species has been discussed by these authors. Hendra, Horder, and Loader (*3c*) concluded that the pyridine, which was strongly held on silica-gel, is bound to the OH groups on the surface and that the degree of interaction with the OH groups was intermediate between that in the pyridine-water system (where there is strong hydrogen bonding) and that in the pyridinium ion, in which complete abstraction of a proton to form $C_5H_5NH^+$ had occurred. Kagel (*7*) also considered that the strongly held pyridine is hydrogen bonded to a silica-gel surface, and interpreted the absence of a strongly adsorbed species in the case of 2-chloropyridine as a consequence of steric hindrance by the bulky chlorine atom.

Our results extend those of previous workers in three ways. First, we have obtained good quality spectra in the 3,000–3,100 cm^{-1} region of the spectrum and have observed all of the main pyridine Raman bands. Second, we have been able to record parallel infrared spectra of the same batch of Cab-O-Sil as was used in the Raman experiments. Third, we have observed spectra from pyridine on porous glass, a silica that is structurally different from the previous two.

Table 4 summarizes the frequencies of environment-sensitive Raman bands of pyridine observed in several solvents using, for

TABLE 4

THE RELATIVE INTENSITIES (I_{1030}/I_{991}), BAND POSITIONS ($\Delta\nu$/CM^{-1}), AND BAND-WIDTHS[a] OF THE C–H STRETCHING AND RING BREATHING FREQUENCIES OF PYRIDINE IN DIFFERENT ENVIRONMENTS[b]

Environment	Nature of the bonding	νCH	Ring breathing modes $\Delta\nu$/cm^{-1}		$\frac{I_{1030}}{I_{991}}$
Pyridine adsorbed on Vycor (275)		3070[a]	1034	1009	0.425
		(14)	(10)	(15)	
Liquid		3058	1030	991	0.75
		(23)	(8)	(7)	
10% solution in CCl_4		3060	1030	991	0.91
		(17)	(7)	(8)	
10% solution in methanol	H-bonded	3062	1029[c]	996	0.28[c]
		(15)	(18)	(8)	
10% solution in water	H-bonded	3072	1035	1002	0.45
		(27)	(8.5)	(10)	
10% solution in HCl	Pyridinium ion	3109	1029	1010	0.34
		(30)	(12)	(15)	
Solid pyridine-oxide[d]	Coordinately bound		1043	1016	0.15

[a] Figures in parentheses are the peak-widths at half the maximum height, ($\delta\nu_{1/2}$/cm^{-1}).

[b] The intensities for adsorbed pyridine were taken from a sample without excess of physically adsorbed species.

[c] Overlap with the 1034 band of liquid methanol.

[d] Data taken from Table 1 of Hendra, Horder, and Loader (*3c*).

comparability, the same slit-widths as were used to obtain spectra from adsorbed pyridine. These measurements supplement those obtained by Hendra, Horder, and Loader (*3c*) in the 1000 cm^{-1} region. Taking into account their results also, it is seen that pyridine molecules in different solvents have bands of comparable intensity in the range 991–1002 cm^{-1}, and 1031–1036 cm^{-1}, the lower band lying in the higher-frequency end of its range when there is considerable hydrogen bonding between pyridine and the solvent. The prominent νCH band falls in the range 3057–3072 cm^{-1}, with again the high frequency end associated with hydrogen-bonding solvents. The pyridinium ion has ranges of 1010–1012 cm^{-1} and 1028–1029 cm^{-1} with the lower frequency band about three times stronger than the other. Our measurement also implies that the pyridinium ion is characterized by a high frequency νCH band near 3110 cm^{-1}. Finally, the earlier data (*3c*) suggest that a coordinate bond between pyridine and a Lewis acid gives rise to frequencies in the 1016–1021 cm^{-1} region (main band) and 1041–1048 cm^{-1} (variable intensity). The Raman bands in the 1000 cm^{-1} region are associated with ring-breathing modes of the pyridine ring, and it is not surprising that these should be fairly sensitive to the bonding to the nitrogen lone-pair.

Taking into account these regularities we conclude that the weakly held species from pyridine on the silicas corresponds to physical adsorption, and that the more strongly held one is better described in terms of strongish hydrogen bonding between silica OH groups and the lone-pair on the nitrogen atom of pyridine, rather than in terms of a proton transfer to form a pyridinium ion. As concluded previously by Parry (*20*), and from our infrared measurements of pyridine on silicas, the absence of pyridinium ions on silica is confirmed by the absence of an infrared band at ca. 1540 cm^{-1} and the OH. . .N hydrogen bond is responsible for the broad infrared band centred near 2900 cm^{-1}. Our conclusions, therefore, are in close agreement with those of Hendra *et al.* (*3*) and Kagel (*7*) and the results of infrared measurements.

Pyridine Adsorption on γ-Alumina and NaY-Zeolite

As previously discussed, we found evidence for three different surface species from the adsorption of pyridine on γ-alumina.

The most strongly held species has its main band at 1018 cm^{-1}. Comparison with the previous discussion on porous silica-gel and Cab-O-Sil suggests that this probably corresponds to a species in which the pyridine molecule forms a coordinate bond through the nitrogen atom, perhaps to surface aluminium atoms.

The species held with intermediate strength has a frequency of 1000 cm^{-1}, and this we tentatively interpret as a species held to the surface by a hydrogen bond between OH groups and the nitrogen lone-pair, which is not as strong as in the case of pyridine hydrogen-bonded to silica. This would be consistent with the observation that the species can be more readily desorbed from the alumina surface than the analogous one from silica. There is infrared evidence (*2*) for several kinds of surface OH groups on γ-alumina, and overal for a greater acidity of the oxide compared with silica. However, there is also infrared evidence that these hydroxyl groups do not interact equally as strong with bases such as ammonia or pyridine. Thus, the breadth of the band centred at 1000 cm^{-1} may result from slightly different hydrogen-bonded species involving more than one type of surface OH group.

The most weakly held species, with its prominent bands at 1032 and 992 cm^{-1}, we ascribe, as in the silica cases, to physically adsorbed pyridine. Hendra, Horder, and Loader (*3c*) made similar assignments of the bands observed for pyridine on γ-alumina. They also pointed out that the Raman conclusions accord well with Parry's infrared conclusions (*20*) that Lewis-acid sites are important on alumina, but not on silica.

Seven bands were observed in the spectrum of pyridine adsorbed on NaY zeolite but only two of these, at 1036 and 1002 cm^{-1}, occurred in the 1000 cm^{-1} region. Of these seven, five were shifted to positions that were more than 5 cm^{-1} higher than the corresponding $\Delta\nu$ of pyridine in the liquid phase. The surface properties of NaY zeolite have been extensively characterized and, although our pretreatment conditions differ from those usually employed, we would expect the surface of the NaY to be relatively nonacidic. The evacuation conditions used in our experiments would have removed almost all of the zeolitic water, and the concentration of hydroxyl groups on the surface of a zeolite is much less than at the surface of an amorphous silica, alumina, or silica-alumina. Therefore, the upward shift in the Raman bands of pyridine adsorbed on NaY zeolite is probably not to be ascribed to hydrogen-bonding. Moreover, it cannot be ascribed to the formation of pyridinium ions.

Ward has shown from infrared studies that pyridine may be coordinated to the cations at the surface of Y zeolites (*21*). The stronger the electrostatic field of the cation, the greater the upward shift in certain vibration frequencies such as for the 1444 and 1580 cm^{-1} infrared bands of adsorbed pyridine. It seems likely that the upward shift of the Raman bands may be due to the same effect. Unpublished Raman spectroscopic studies carried out in this laboratory with other zeolites show that the Raman shifts do vary with the type of charge-balancing cation that is present.

Other Molecules Adsorbed on Porous Glass

Benzene

Infrared studies of adsorption on porous glass have shown that the surface hydroxyl groups are perturbed by the adsorption of benzene (*1*). The stretching frequency of the Si-OH is lowered by about 120 cm^{-1} and this is interpreted as a consequence of the interaction of the π electrons of adsorbed molecules with the surface hydroxyl groups. Similar results have been reported for benzene adsorption on Aerosil by Galkin, Kiselev, and Lygin (*22*). Both studies found that the positions of the infrared bands of benzene were altered very little by hydrogen-bonding to surface hydroxyls. Even the out-of-plane CH deformation mode, which is particularly sensitive to changes in the π electron distribution (*23*), shifted upward by only 10 wavenumbers. It is not surprising, therefore, to find that the Raman bands of adsorbed benzene are close in position to those of the liquid. However, as has been noted above, the relative intensities of the Raman bands of the adsorbed species are different from those in the liquid spectrum. In particular, the intensity of the 994 cm^{-1} band is decreased relative to the other bands in the spectrum of the adsorbed benzene. The 994 cm^{-1} band is assigned to the ring breathing mode of the benzene molecule, and the decrease in its intensity is consistent with a lowered polarizability of the ring electrons, which is an expected consequence of their interaction with surface hydroxyls. At higher coverages the hydrogen-bonded molecules make a smaller contribution to the overall spectrum, and the relative intensity of the 994 cm^{-1} band increases again.

The unusual changes in the relative intensities of the C–H stretching bands with coverage discussed in the Results section cannot be interpreted with certainty. We tentatively suggest that these changes may be a consequence of the pores in the porous glass structure. These have been likened to a set of spherical pores that are connected by narrow channels (*24, 25*). It has been suggested (*24*) that two superimposed adsorbed benzene molecules would fit very tightly in the narrow channels and that this would lead to increased adsorbate–adsorbate interaction. At low coverages, the effect would not be important; at intermediate coverages the narrow channels could become "clogged" by interacting benzene molecules and these could then prevent further entry of molecules into the sperical pores. According to this picture only at higher relative pressures would the molecules in the narrow channels be able to empty into the spherical pores, and thus release the tight packing of the benzene molecules in the narrow channels. During the desorption of benzene, there is no stage at which the molecules are compressed together in the connecting channels, and this may be why we do not observe the changed relative intensities of the CH stretching band.

It is relevant to note that Cusamano and Low (*25*) have found that the ratio of the extinction coefficients of the 3040 and 3090 cm^{-1} infrared adsorptions of adsorbed benzene decreased with increasing coverages of benzene.

Aniline

Aniline adsorption on porous glass resulted in slight upward shifts of most bands in the Raman spectrum. The exception was a downward shift, from 1279 to 1262 cm^{-1}, of the band assigned as a substituent-sensitive mode in monosubstituted benzenes with a considerable proportion, in the case of aniline, of C–N bond-stretching character. The relative intensities of the 1007 and 1028 cm^{-1} bands were unaffected by a fourfold change in coverage.

Aniline is expected to hydrogen bond, via the amino group, to surface hydroxyls on porous glass. Infrared studies have shown that when aniline is adsorbed on Aerosil the νOH frequency shifts down by about 550 cm^{-1} (cf. 750 cm^{-1} for pyridine) (*26*). However, presumably because the nitrogen of aniline is outside the ring, the hydrogen bonding has rather little effect on the Raman spectrum, which is dominated by bands associated with the ring vibrations. The vibrations associated with the N–H stretching fall at about 3,400 cm^{-1} and could not be observed because of the fall in photomultiplier sensitivity in this region.

Benzylamine and Chlorobenzene

In the case of benzylamine, the amino group is even further from the aromatic ring and the effects of hydrogen bonding are smaller than in the case of aniline. Thus, the 996 cm^{-1} band of aniline was shifted upwards by 5 cm^{-1} on adsorption, whereas the corresponding band of benzylamine occurs at 1003 cm^{-1} and is only perturbed by 1 cm^{-1} upon adsorption.

In the case of chlorobenzene, we may expect yet weaker hydrogen bonding through the chlorine atom, and it is not surprising that the liquid and adsorbed spectra are almost identical. Even the C–Cl stretching mode is only slightly changed in relative intensity.

It will be noticed that the above studies on porous glass have not shown any evidence for the formation of species adsorbed on the small proportion of boron sites in the porous glass.

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