

IR Spectroscopic Investigation of the Interaction of Quinoline with Acidic Sites on Oxide Surfaces

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IR spectra of quinoline have been measured following adsorption on and subsequent desorption from SiO_2 , TiO_2 , ZrO_2 , niobic acid, $\text{SiO}_2\text{-Al}_2\text{O}_3$, H-mordenite, and sepiolite. There is clear evidence from the IR spectra of three modes of adsorption: (i) hydrogen bonding to surface hydroxyl groups, (ii) electron transfer at Lewis acidic surface sites, and (iii) proton transfer at Brønsted acidic surface sites. Protonation of quinoline occurred with adsorption on niobic acid, $\text{SiO}_2\text{-Al}_2\text{O}_3$, and H-mordenite, indicating the presence of Brønsted acidic sites with $\text{p}K_a$ values ≤ 4.90 . Hydrogen bonding and interaction with Lewis acid sites was observed for each of the oxides studied. The results establish that the adsorption of quinoline can provide useful information regarding the nature of surface acidity on oxides which is complementary to that obtained from other probe molecules such as NH_3 and pyridine.

Introduction

The acidity of oxide surfaces has been subjected to intensive study owing to its importance in heterogeneous catalysis. A detailed characterization of surface acidity requires the determination of the density of acid sites, the nature of acid sites (i.e., Brønsted and Lewis), and their acid strengths. Many techniques have been developed for the characterization of surface acidity, yet no single technique can yield both a quantitative and qualitative determination of the surface acidity. Hence, a number of methods have been employed, the majority of which involve either some form of titration with a base under aqueous, nonaqueous, or gas-phase conditions^{1–4} or measurements based upon activity and selectivity toward some particular catalytic reaction.^{5–7} Among these, IR spectroscopy of adsorbed nitrogen bases (especially NH_3 and pyridine) on acidic surfaces has become established as an accurate and reliable method for determining the nature of the individual sites present.

To quantify the strengths of acidic sites using IR spectroscopy in conjunction with probe molecules, it is necessary to adsorb a variety of probe molecules whose conjugate acids span a wide range of $\text{p}K_a$ values. With this objective in mind, we have surveyed a number of heterocyclic nitrogen bases and their adsorption on oxide surfaces. In the present paper, we report results obtained for quinoline, for which the $\text{p}K_a$ value of the quinolinium ion is 4.90; thus, protonation is expected on both weak and strongly acidic surface sites. Quinoline is a planar molecule (C_s symmetry) with 45 normal modes and the IR spectrum has been reported by Wait and McNerney.⁸ We

have studied the adsorption of quinoline on a range of oxides which exhibit (a) no surface acidity (SiO_2) and (b) Lewis acidity (TiO_2 and ZrO_2) and Brønsted acidity ($\text{SiO}_2\text{-Al}_2\text{O}_3$, H-mordenite and sepiolite).

Experimental Section

Quinoline (Aldrich, 98%) was purified by distillation. IR spectra of liquid quinoline and quinolinium chloride were obtained from films within sodium chloride windows. The oxides used in this study and details of their pretreatment are summarized in Table 1. 80 mg of each oxide was pressed into a self-supporting disk of 1-in. diameter at a pressure of 80 MN m^{-2} . This was treated under a flow of dry air (100 $\text{cm}^3 \text{min}^{-1}$) for 1 h, followed by evacuation for 1 and 17 h at 500 °C. The IR spectrum was recorded after treatment. The sample was exposed to small aliquots of quinoline vapor, and IR spectra were recorded first on adsorption as a function of increasing surface coverage, and second on desorption as a function of evacuation time.

IR spectra of disks at ca. 293 K were recorded using a Perkin-Elmer 1710x FTIR spectrophotometer interfaced to a Perkin-Elmer series 7770 computer. The spectra were acquired at a resolution of 4 cm^{-1} . The CaF_2 windows of the cell restricted the wavenumber range to a lower limit of 1000 cm^{-1} . All spectra are presented in absorbance mode, following subtraction of the spectrum of the oxide surface prior to adsorption.

Results

Quinoline and the Quinolinium Cation. IR spectra of liquid quinoline and the quinolinium cation, in the region 1000–1700 cm^{-1} , are displayed in Figure 1, and the band positions and assignments are listed in Table 2. The band assignments were deduced from ab initio calculations at the B3-LYP/DZ++ level using the *Gaussian 98* program⁹ and normal coordinate analysis programs. A

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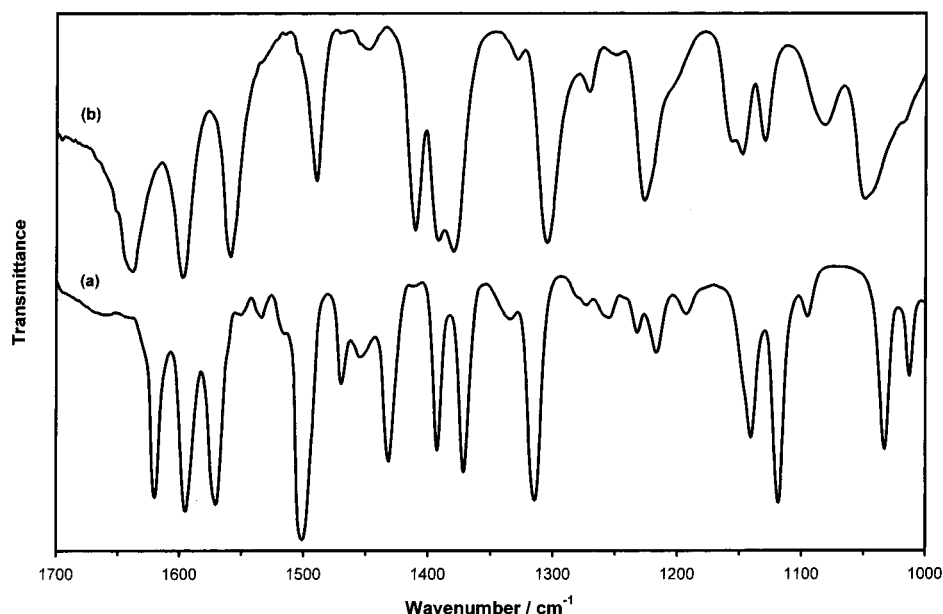


Figure 1. IR spectra of (a) quinoline and (b) quinolinium chloride.

Table 1. Oxides Used in this Study

oxide	source	surface area/m ² g ⁻¹	pretreatment temperature/ °C
SiO ₂	Cab-o-Sil M5	200	500
TiO ₂ (anatase)	P25 Degussa AG	58.7	(a) 450 (b) 200
ZrO ₂	SiO ₂ -stabilized XZO 645 Mel Chemicals	99.6	400
Niobic acid	AD-317 Companhia Brasileira de Metallurgia e Mineração	119	100
SiO ₂ Al ₂ O ₃	Aldrich Grade 135, 13% Al ₂ O ₃	475	500
<i>H</i> -mordenite	EZ-321 Engelhard	478	500
Sepiolite	Tolsa	145.8	400

Table 2. Experimental and Calculated Vibrational Fundamentals for Quinoline and the Quinolinium Cation

quinoline			quinolinium cation		
exp.	calc.	assignment	exp.	calc.	assignment
1620	1632	$\nu(\text{CC/CN})$ [B _{3g}]	1638	1634	$\nu(\text{CC/CN})$ [B _{3g}]
1595	1594	$\nu(\text{CC/CN})$ [B _{1u}]	1597	1594	$\nu(\text{CC/CN})$ [A _g]
1570	1562	$\nu(\text{CC/CN})$ [A _g]		1583	$\nu(\text{CC/CN})$ (B _{1u})
1501	1493	$\nu(\text{CC})$ [B _{2u}]	1559	1551	$\nu(\text{CC}), \delta_{\text{ip}}(\text{CH}), \delta_{\text{ip}}(\text{NH})$ [B _{2u}]
1469	1444	$\nu(\text{CC/CN}), \delta(\text{CCC/NCC}), \delta_{\text{ip}}(\text{CH})$ [B _{3g}]	1489	1467	$\delta_{\text{ip}}(\text{CH}), \delta_{\text{ip}}(\text{NH})$
1431	1419	$\nu(\text{CC/CN}), \delta_{\text{ip}}(\text{CH})$ [A _g]	1448	1443	$\nu(\text{CC/CN}), \delta(\text{CCC/NCC}), \delta_{\text{ip}}(\text{CH})$ [B _{3g}]
1392	1388	$\nu(\text{CC}), \delta_{\text{ip}}(\text{CH})$ [A _g]	1410	1418	$\nu(\text{CC/CN})$ [A _g]
1371	1363	$\nu(\text{CC}), \delta_{\text{ip}}(\text{CH})$ [B _{1u}]	1392	1387	$\nu(\text{CC}), \delta_{\text{ip}}(\text{CH})$ [B _{1u}]
1314	1330	$\nu(\text{CC/CN}), \delta_{\text{ip}}(\text{CH})$ [B _{2u}]	1379	1380	$\nu(\text{CC/CN}), \delta_{\text{ip}}(\text{NH})$ [B _{2u}]
			1329	1302	$\nu(\text{CC}), \delta_{\text{ip}}(\text{CH}), \delta_{\text{ip}}(\text{NH})$ [B _{1u}]
1255	1251	$\delta(\text{CCC/NCC}), \delta_{\text{ip}}(\text{CH})$ [B _{3g}]	1271	1266	$\delta_{\text{ip}}(\text{CH})$
1216	1222	$\nu(\text{CC}), \delta_{\text{ip}}(\text{CH})$ [B _{1u} , B _{2u}]	1226	1235	$\nu(\text{CC}), \delta_{\text{ip}}(\text{CH})$ [B _{2u}]
1193	1210	$\nu(\text{CC}), \delta_{\text{ip}}(\text{CH})$ [B _{2u}]	1206	1207	$\delta_{\text{ip}}(\text{CH})$
1140	1146	$\delta_{\text{ip}}(\text{CH})$	1155	1169	$\delta_{\text{ip}}(\text{CH})$
1118	1131	$\nu(\text{CC/CN}), \delta_{\text{ip}}(\text{CH})$ [B _{3g}]	1148	1147	$\nu(\text{CC/CN}), \delta_{\text{ip}}(\text{CH})$ [B _{3g}]
1095	1105	$\nu(\text{CC/CN}), \delta(\text{CCC}), \delta_{\text{ip}}(\text{CH})$ [B _{1u}]	1130	1125	$\nu(\text{CC/CN}), \delta(\text{CCC}), \delta_{\text{ip}}(\text{CH})$ [B _{1u}]
1033	1024	$\nu(\text{CC}), \delta(\text{CCC})$ [A _g]	1049	1048	$\nu(\text{CC/CN}), \delta(\text{CCC})$ [A _g]
1013	1010	$\nu(\text{CC/CN})$ [B _{2u}]	1018	1016	$\nu(\text{CC/CN})$ [B _{2u}]

best fit to the experimental spectra was determined by force constants expressed in internal coordinates, f_{ij} , by the formula

$$f_{ij}^{\text{scaled}} = f_{ij}^{\text{calc}} \sqrt{s_i s_j}$$

where the scaling factors s_i and s_j were set at 0.90 for CH and NH stretches; 0.97 for CC and CN stretches; 0.91 for CCH, NCH, and CNH deformations; 0.95 for other in-plane deformations; and 0.88 for all out-of-plane deformations. The symmetry species given in the assignments are those relating to the equivalent vibrations in naphthalene, as reported by Wait and McNerney.⁸

Adsorption on SiO₂. The adsorption of quinoline on SiO₂ results in the decrease in intensity of the IR band of SiO₂ at 3746 cm⁻¹ attributed to free surface hydroxyl groups, with a concomitant increase of a broad band at 3410 cm⁻¹ because of perturbed hydroxyl groups involved in a hydrogen-bonding interaction with quinoline. Bands arising from $\nu(\text{CH})$ modes of adsorbed quinoline occur at 3013 and 2970 cm⁻¹. In the quinoline ring vibration region (Figure 2), the IR spectrum after the initial adsorption of quinoline is relatively simple, exhibiting bands at 1508, 1425, and 1372 cm⁻¹. With increasing coverage, a weak band appears at 1582 cm⁻¹ and all bands become progressively stronger. Upon evacuation, the broad band

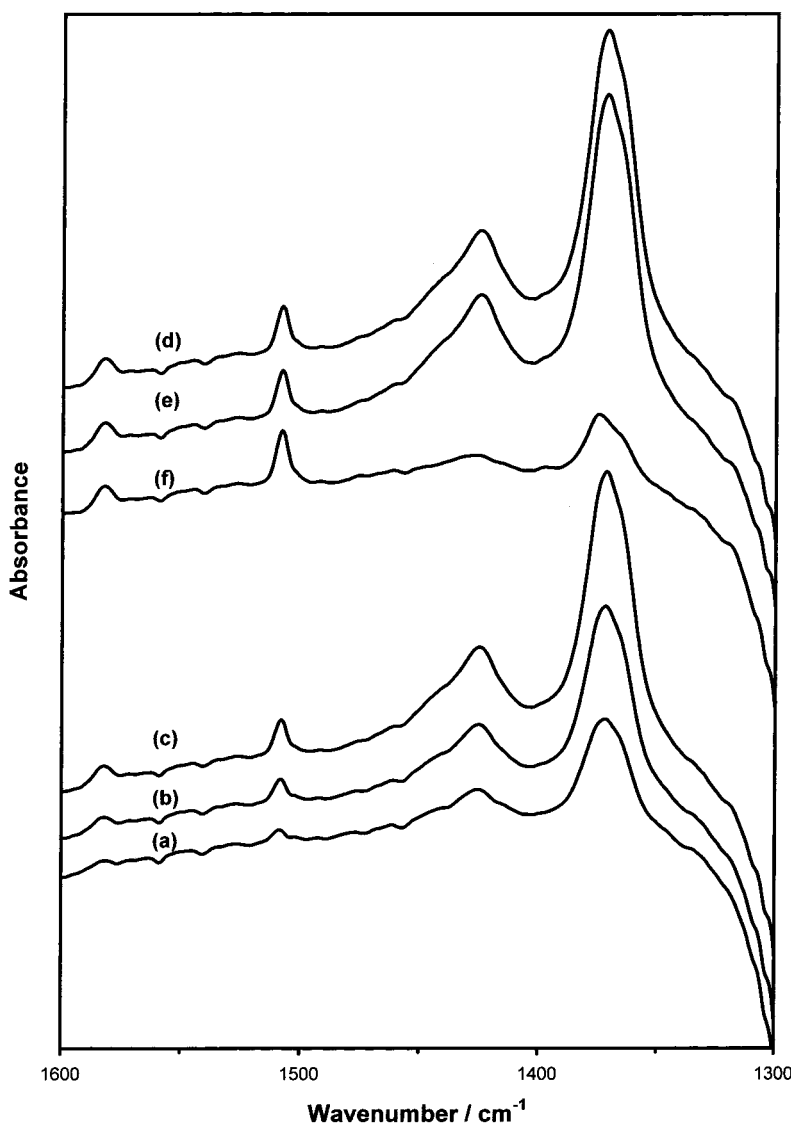


Figure 2. IR spectra of quinoline on SiO₂ at increasing coverage (a) to (c) and following evacuation at room temperature (d) immediately, (e) 1 h, and (f) overnight.

at 3410 cm⁻¹ and the $\nu(\text{CH})$ bands decrease in intensity and eventually disappear. However, the 1582 and 1508 cm⁻¹ bands do not decrease in intensity during evacuation, and these are assigned to chemisorbed quinoline. The bands at 1372 and 1425 cm⁻¹, which become much less intense during evacuation, are ascribed to hydrogen-bonded quinoline.

Adsorption on TiO₂. The IR spectra of quinoline adsorbed on TiO₂ are more complex, providing evidence for rather different behavior from that observed following adsorption on SiO₂. Prior to quinoline adsorption, the IR spectrum of TiO₂ exhibits two $\nu(\text{OH})$ bands at 3720 and 3672 cm⁻¹. On adsorption of quinoline these bands disappear, to be replaced by a broad band at 3404 cm⁻¹ and a $\nu(\text{CH})$ band at 2972 cm⁻¹. In the quinoline ring vibration region (Figure 3), initial adsorption results in a strong band at 1367 cm⁻¹, a band at 1509 cm⁻¹, and a weak doublet at 1584, 1599 cm⁻¹. With increasing coverage, there are several changes: the 1599 cm⁻¹ band becomes stronger at the expense of the 1584 cm⁻¹ band, new bands appear at 1448 and 1436 cm⁻¹, and the 1509 and 1367 cm⁻¹ bands become stronger. Eventually, further bands appear at 1621 and 1317 cm⁻¹, the band at 1599 cm⁻¹ weakens, and the strong band at 1367 cm⁻¹ shifts to 1364 cm⁻¹. In the lower wavenumber region, initial

adsorption of quinoline produces a strong band at 1238 cm⁻¹; medium intensity bands at 1197 and 1138 cm⁻¹; and weaker bands at 1167, 1094, and 1053 cm⁻¹, none of which become stronger with increasing coverage. The 1238 cm⁻¹ band decreases in intensity, the band at 1197 cm⁻¹ shifts to 1203 cm⁻¹, and the 1138 cm⁻¹ band shifts to 1141 cm⁻¹. The 1167 cm⁻¹ band disappears with increasing coverage. On evacuation, the broad band at 3404 cm⁻¹ is removed although the bands at 3720 and 3672 cm⁻¹ are not regenerated. The $\nu(\text{CH})$ band at 2972 cm⁻¹ decreases in intensity and a new band appears at 3069 cm⁻¹, attributed to a $\nu(\text{CH})$ mode of coordinated quinoline. The band at 1622 cm⁻¹ intensifies slightly on evacuation and the 1599 cm⁻¹ band splits into a well-resolved doublet at 1599, 1584 cm⁻¹, ascribed to ligated quinoline. The 1509 cm⁻¹ band, attributed to coordinated quinoline, becomes relatively much stronger with prolonged evacuation and becomes the strongest band in this region. The bands at 1446 and 1436 cm⁻¹, which remain after evacuation overnight, and the 1365 cm⁻¹ band are ascribed to quinoline chemisorbed at electron deficient titanium atoms acting as Lewis acid sites, as also is the 1317 cm⁻¹ band, which becomes relatively more intense with prolonged evacuation. The intensity distribution in the lower spectral region is restored to that observed in the spectrum recorded

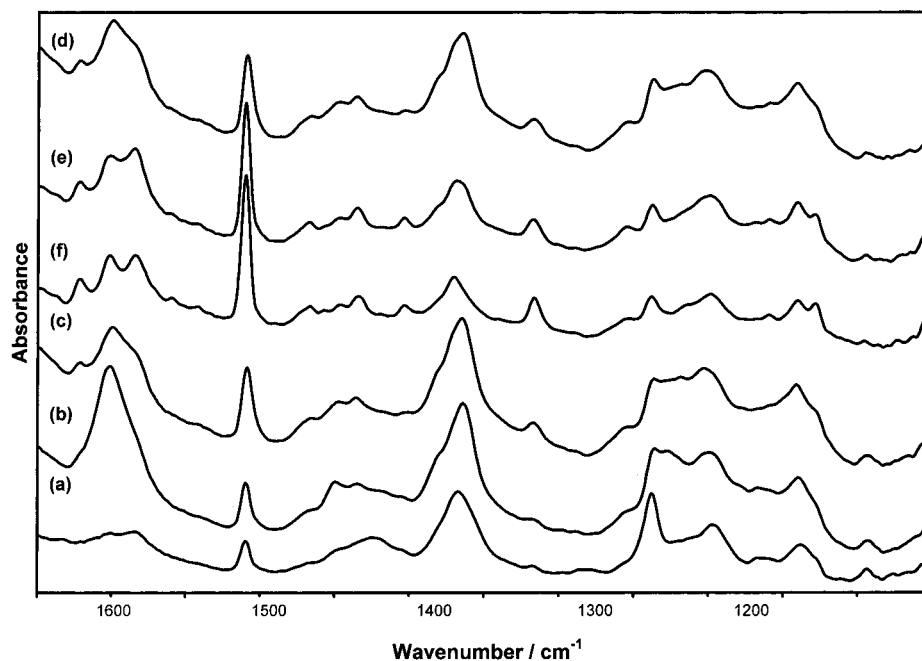


Figure 3. IR spectra of quinoline on TiO_2 at increasing coverage (a) to (c) and following evacuation at room temperature (d) immediately, (e) 1 h, and (f) overnight.

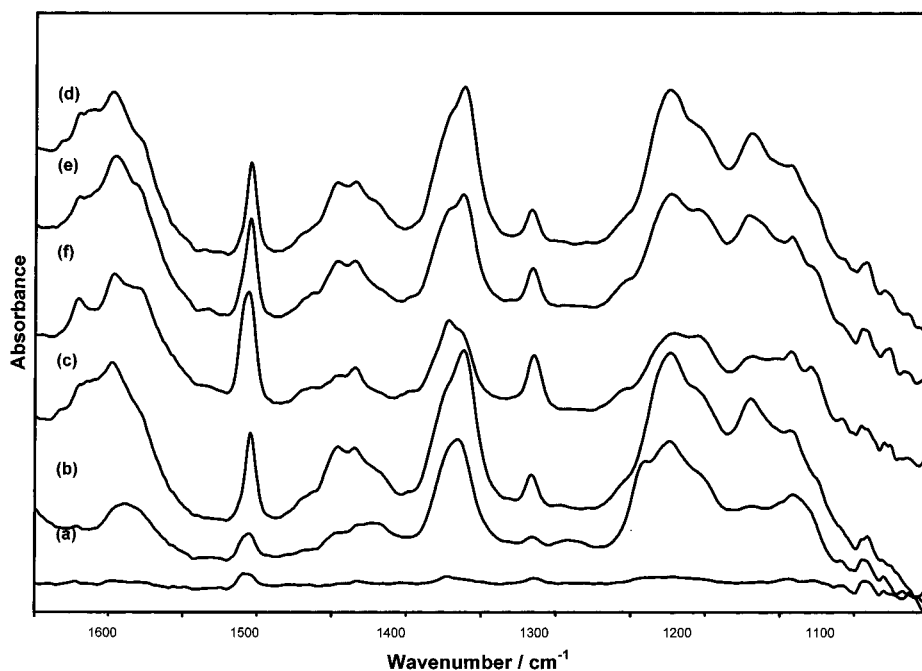


Figure 4. IR spectra of quinoline on ZrO_2 at increasing coverage (a) to (c) and following evacuation at room temperature (d) immediately, (e) 30 min, and (f) overnight.

after initial adsorption of quinoline, except for the appearance of a doublet at 1140, 1129 cm^{-1} . These bands are assigned to in-plane C–H deformations of quinoline chemisorbed at Lewis acid sites. The band at 1053 cm^{-1} is assigned to the ring-breathing vibration of coordinated quinoline, although it is substantially shifted from its position in the IR spectrum of liquid quinoline (1033 cm^{-1}).

Adsorption on ZrO_2 . The IR spectra of quinoline adsorbed on ZrO_2 , shown in Figure 4, closely resemble those observed following adsorption on TiO_2 . A band at 1598 cm^{-1} grows at the expense of the 1588 cm^{-1} band but, unlike the results observed for adsorption on TiO_2 , the 1598 cm^{-1} band does not decrease in intensity with increasing coverage. The 1509 cm^{-1} band becomes stronger with increasing coverage and shifts to 1505 cm^{-1} , and a

doublet at 1446, 1435 cm^{-1} becomes better resolved. The strong band at 1366 cm^{-1} intensifies and shifts to 1362 cm^{-1} , and the 1317 cm^{-1} band also increases in intensity. There are fewer resemblances with the quinoline/ TiO_2 spectrum in the lower wavenumber region, where there are bands at 1224, 1170, and 1091 cm^{-1} which become stronger with increasing coverage and a band at 1141 cm^{-1} which weakens. After prolonged evacuation, a new band appears at 1621 cm^{-1} , ascribed to ligated quinoline. The 1588 cm^{-1} band is not restored on evacuation, as was found for quinoline/ TiO_2 , but instead appears as a shoulder on the 1597 cm^{-1} band. The 1507 cm^{-1} band intensifies slightly after overnight evacuation but not to the same extent as in the quinoline/ TiO_2 spectra. The relative intensities of the doublet at 1446 and 1435 cm^{-1} are

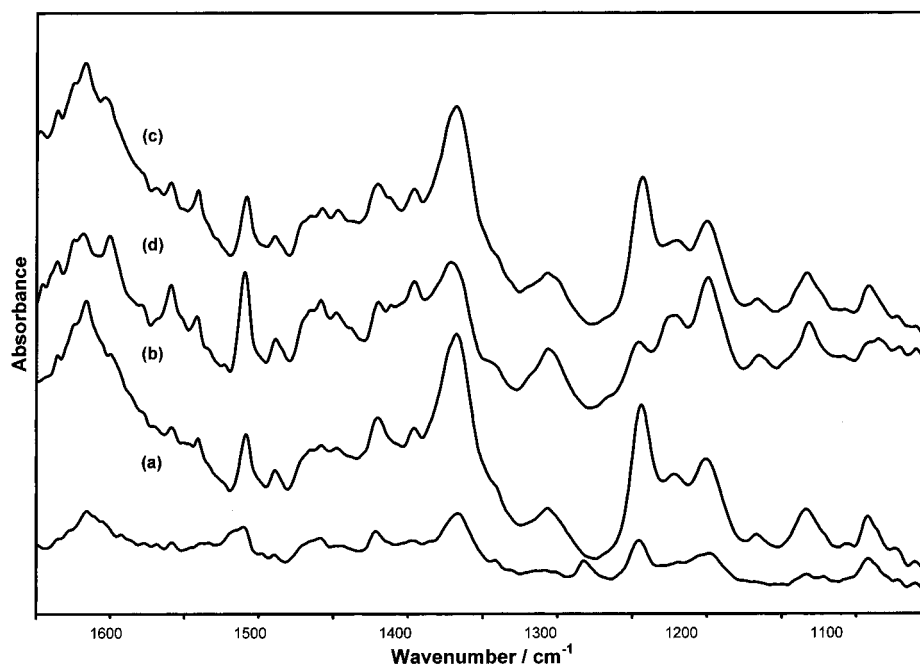


Figure 5. IR spectra of quinoline on niobic acid at increasing coverage (a) and (b) and following evacuation at room temperature (c) immediately and (d) overnight.

inverted during evacuation, and the 1446 cm^{-1} band disappears after prolonged evacuation. The band at 1362 cm^{-1} decreases in intensity and shifts to 1372 cm^{-1} and the band at 1317 cm^{-1} becomes stronger, both bands are attributed to ring vibrations of quinoline coordinated to Lewis acid sites. Desorption of quinoline results in the decrease in intensity of most of bands in the $1300\text{--}1000\text{ cm}^{-1}$ region. The 1225 cm^{-1} band decreases in intensity and splits into a weak doublet at $1221, 1207\text{ cm}^{-1}$, and the band at 1170 cm^{-1} also becomes much weaker. These bands are assigned to in-plane C–H deformations of quinoline chemisorbed at electron deficient zirconium atoms acting as Lewis acid sites. By contrast, the 1143 cm^{-1} band becomes relatively stronger on evacuation and a new band appears at 1130 cm^{-1} ; these bands are also attributed to chemisorbed quinoline (A_g).

Adsorption on Niobic Acid. Initially, adsorption of quinoline on niobic acid exhibits prominent IR bands at $1616, 1510, 1458, 1422,$ and 1367 cm^{-1} and very weak bands at 1559 and 1395 cm^{-1} (Figure 5). The $1616, 1510, 1422,$ and 1367 cm^{-1} bands all become stronger with increasing coverage; the 1422 cm^{-1} band shifts to 1420 cm^{-1} ; and the 1458 cm^{-1} band splits into a very weak doublet at $1458, 1447\text{ cm}^{-1}$. New bands appear at 1489 and 1307 cm^{-1} . In the lower wavenumber spectral region, bands initially appear at $1282, 1246, 1199,$ and 1092 cm^{-1} , with a weak doublet at $1133, 1122\text{ cm}^{-1}$. The $1246, 1199,$ and 1092 cm^{-1} bands become stronger with increasing coverage; the doublet merges into a single band at 1134 cm^{-1} ; and new bands appear at 1222 and 1167 cm^{-1} . Following evacuation, the 1617 cm^{-1} band splits into a doublet at $1619, 1601\text{ cm}^{-1}$, of which the former is assigned ascribed to a ring-stretching vibration of chemisorbed quinoline and the latter to a ring-stretching vibration of the quinolinium ion. The bands at 1559 and 1489 cm^{-1} , which become relatively stronger after overnight evacuation, are attributed to ring-stretching modes of the quinolinium ion. Other bands which increase in intensity during desorption are those at $1508, 1396,$ and 1307 cm^{-1} . The 1508 cm^{-1} band is attributed to a ring-stretching vibration of quinoline chemisorbed at Lewis acid sites, and the bands at 1396 and 1307 cm^{-1} are attributed to

ring vibrations of the quinolinium ion. Upon prolonged evacuation, the bands at 1421 and 1368 cm^{-1} decrease in intensity and the 1368 cm^{-1} band shifts to 1372 cm^{-1} . These bands are assigned to ring vibrations of quinoline chemisorbed at Lewis acid sites, as also are weak bands at 1459 and 1447 cm^{-1} which remain even after overnight evacuation. In the lower wavenumber spectral region, the band at 1200 cm^{-1} becomes relatively stronger during evacuation but the $1222, 1166,$ and 1132 cm^{-1} bands remain unchanged. These bands were also found in the spectra of quinoline adsorbed on TiO_2 and ZrO_2 and are assigned to in-plane C–H deformations of chemisorbed quinoline. The bands at 1246 and 1085 cm^{-1} , which were not found in the spectra of quinoline adsorbed on TiO_2 and ZrO_2 , are assigned to in-plane C–H deformations of quinolinium ions. A band at 1036 cm^{-1} , which disappears upon evacuation, is believed to be the totally symmetric ring-breathing mode of hydrogen-bonded quinoline.

Adsorption on $\text{SiO}_2\text{--Al}_2\text{O}_3$. The IR spectrum of $\text{SiO}_2\text{--Al}_2\text{O}_3$ displays a band at 3735 cm^{-1} attributed to isolated silanol groups, which disappears on adsorption of quinoline and is not restored after evacuation. In the quinoline ring vibration region (Figure 6), initial adsorption produces bands at $1603, 1517,$ and 1380 cm^{-1} . With increasing coverage, the following changes occur: (i) a doublet appears at $1516, 1507\text{ cm}^{-1}$ and new bands appear at 1397 and 1316 cm^{-1} , (ii) the relative intensities of the doublet become inverted and new bands appear at 1567 and 1435 cm^{-1} , and (iii) the 1381 and 1397 cm^{-1} bands become stronger and the 1317 cm^{-1} band becomes weaker. Upon evacuation, the bands at $1601, 1565, 1381,$ and 1315 cm^{-1} become relatively stronger; there is inversion of the relative intensities of the doublet at $1516, 1507\text{ cm}^{-1}$ and a new band appears at 1412 cm^{-1} . Following prolonged evacuation, the 1435 cm^{-1} band shifts to 1442 cm^{-1} . The $1601, 1565, 1413, 1397,$ and 1381 cm^{-1} bands are attributed to ring-stretching vibrations of the quinolinium ion. The remaining bands, at 1442 and 1315 cm^{-1} and the doublet at $1517, 1506\text{ cm}^{-1}$, are ring vibrations of coordinated quinoline.

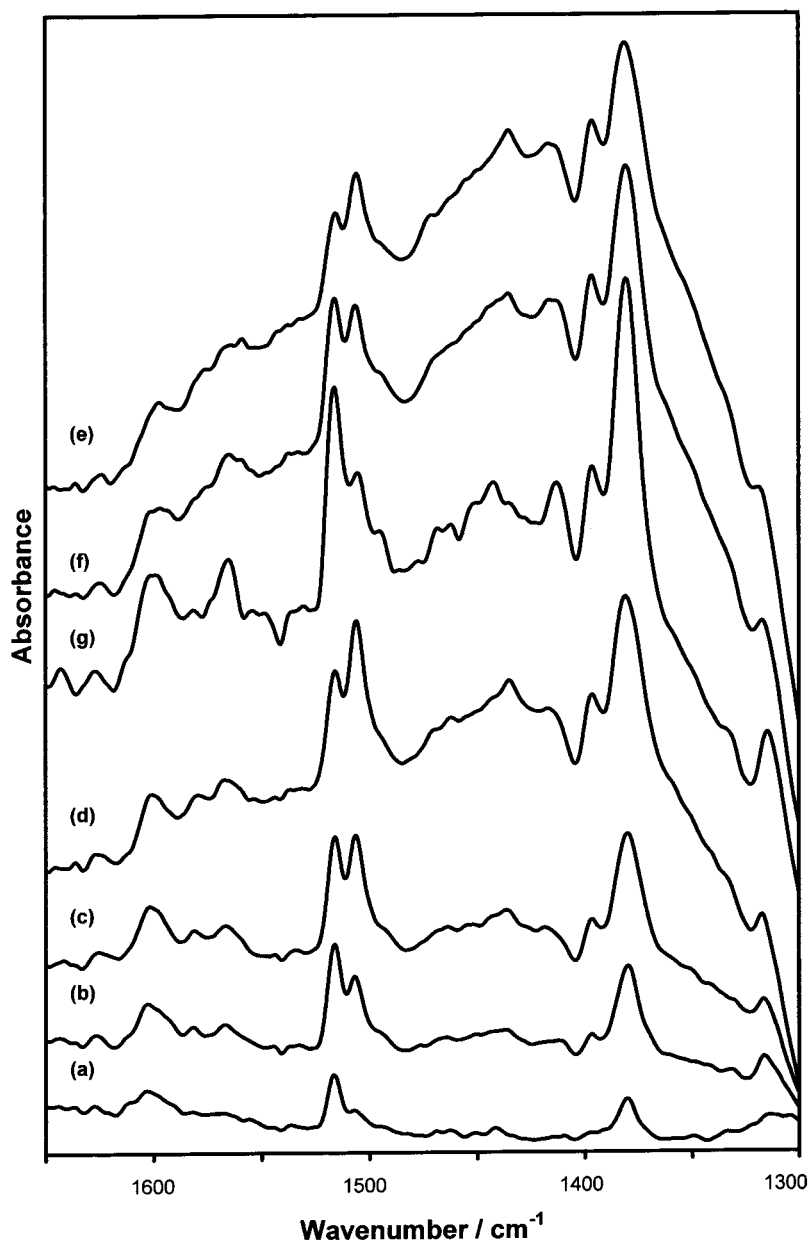


Figure 6. IR spectra of quinoline on $\text{SiO}_2\text{-Al}_2\text{O}_3$ at increasing coverage (a) to (d) and following evacuation at room temperature (e) immediately, (f) 90 min, and (g) overnight.

Adsorption on *H*-Mordenite. The IR spectra of quinoline adsorbed on *H*-mordenite are shown in Figure 7. Initially, there are bands at 1600, 1565, 1413, and 1379 cm^{-1} , which become stronger with increasing coverage, and further bands appear at 1644, 1581, 1506, 1494, and 1396 cm^{-1} . On evacuation, the bands at 1644, 1600, 1565, 1494, 1413, 1396, and 1379 cm^{-1} become relatively stronger and a new band appears at 1306 cm^{-1} . The bands at 1581 and 1505 cm^{-1} , which disappear after evacuation for 2 h, are assigned to ring-stretching vibrations of weakly chemisorbed quinoline. The bands at 1644, 1600, 1565, 1494, 1413, 1396, 1379, and 1306 cm^{-1} are attributed to ring stretching and deformation vibrations of the quinolinium ion.

Adsorption on Sepiolite. The IR spectrum of sepiolite sample displays four bands in the $\nu(\text{OH})$ region, attributed to SiOH groups (3723 cm^{-1}), MgOH groups (3671 cm^{-1}), and the antisymmetric and symmetric stretches of molecular water (3605 and 3530 cm^{-1}). All of these bands remain after adsorption of quinoline. In the quinoline ring vibration region, the IR spectrum (Figure 8) initially

displays bands at 1615, 1508, 1442, 1374, and 1247 cm^{-1} . With increasing coverage, the 1615 cm^{-1} band disappears and the bands at 1508, 1420, and 1374 cm^{-1} become stronger. The 1247 cm^{-1} band becomes stronger and shifts to 1240 cm^{-1} . On evacuation, the $\nu(\text{OH})$ bands become relatively stronger and the band at 1598 cm^{-1} , attributed to chemisorbed quinoline, disappears or is more likely masked by the strong broad band at 1615 cm^{-1} . The latter is due to the deformation of molecular water. The 1508 cm^{-1} band becomes relatively stronger and shifts to 1511 cm^{-1} , the 1420 cm^{-1} band is removed, and the 1374 cm^{-1} band weakens. The band at 1240 cm^{-1} , which is assigned to a sepiolite Si-O-Si vibration, weakens in intensity and shifts to 1244 cm^{-1} .

Discussion

Adsorption on SiO_2 . At temperatures above 400 $^\circ\text{C}$, SiO_2 becomes hydrophobic and resistant to rehydroxylation and the surface possesses freely vibrating silanol groups and siloxane bridges.¹⁰ Heating to higher temperatures can result in Lewis reactive siloxane bridge sites

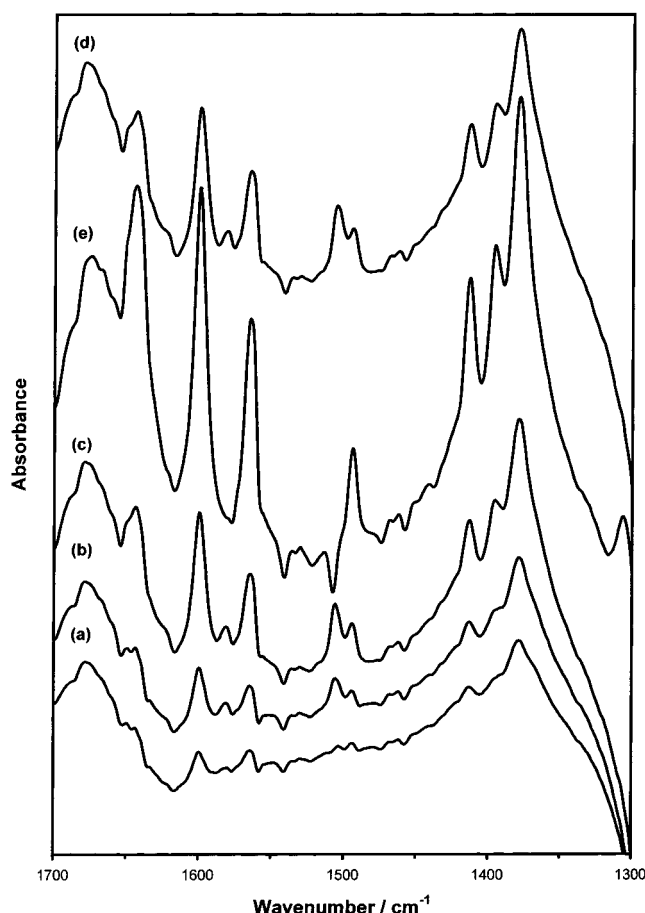


Figure 7. IR spectra of quinoline on *H*-mordenite at increasing coverage (a) to (c) and following evacuation at room temperature (d) immediately and (e) overnight.

being generated. Morrow and Cody^{11,12} have demonstrated that these sites are capable of dissociatively chemisorbing NH_3 , H_2O , and CH_3OH . Weak Brønsted acidity has been reported on SiO_2 ^{13,14} although these sites do not possess adequate strength to protonate pyridine or NH_3 ¹⁵, and SiO_2 is not therefore expected to behave as a Brønsted acid in the presence of quinoline. There is evidence for hydrogen bonding between quinoline and surface hydroxyl groups, and the adsorbed quinoline is readily removed upon evacuation. It is known that pyridine undergoes hydrogen bonding with surface hydroxyl groups through the nonbonding electron pair on the nitrogen atom, and it is believed that this is also the case for quinoline. Since the intensities of the 1582 and 1508 cm^{-1} bands are unchanged by prolonged evacuation, these are assigned to ring-stretching vibrations of ligated quinoline. It is proposed that the interaction involves coordination of quinoline through the nonbonding electron pair on the nitrogen atom to electron deficient silicon atoms acting as Lewis acid sites. Thus, quinoline reacts with the SiO_2 surface in two identifiable ways. The absence of a band attributable to $\nu(\text{NH})$ clearly indicates that, on adsorption on SiO_2 , quinoline is not protonated.

Adsorption on TiO_2 . The TiO_2 surface exhibits two $\nu(\text{OH})$ bands in the IR spectrum at 3725 and 3670 cm^{-1} ¹⁶ which disappear on adsorption of quinoline with the appearance of a broad band centered at 3400 cm^{-1} . The magnitude of the wavenumber shift $\Delta\nu(\text{OH})$ induced by quinoline adsorption is greater than that observed for quinoline adsorbed on SiO_2 , indicating that a stronger hydrogen-bonding interaction occurs between quinoline molecules and surface Ti–OH groups than with Si–OH groups, although these spectral changes are reversed on evacuation at ambient temperature. In the quinoline ring vibration region, initial adsorption results in the appearance of bands at 1600, 1584, 1509, and 1367 cm^{-1} which are attributed to interactions with Lewis acid sites. Furthermore, the appearance of the 1425 cm^{-1} band at low surface coverage demonstrates that TiO_2 also functions as a donor involved in hydrogen bonding. Further adsorption, in the ring vibration region, affords evidence that only Lewis acid type interaction exists.

Studies involving pyridine adsorption on TiO_2 have shown that the shift in the 8a ring vibration of ligated pyridine during desorption (1600 to 1615 cm^{-1}) indicates the presence of two types of Lewis acid sites on the TiO_2 surface, attributed to surface Ti atoms in different states of coordinative unsaturation,^{17,18} although the spectra of adsorbed quinoline do not enable distinction between the two sites. At high surface coverage, bands are observed at 1600 and 1621 cm^{-1} of which the former is more intense but decreases in intensity during evacuation, while the relative intensity of the 1621 cm^{-1} band increases during evacuation. This behavior may indicate quinoline adsorbed on Lewis acid sites of different strengths, where prolonged evacuation would result in the preferential desorption of the species responsible for the 1600 cm^{-1} band. Desorption also results in the considerable increase in relative intensity of the 1509 cm^{-1} band, indicating a stronger Lewis acid site on TiO_2 than on SiO_2 . The spectra in the ring vibration region show there to be a greater density Lewis acid sites on TiO_2 , that are accessible to quinoline, than on SiO_2 . In the lower wavenumber region, the broadness of some bands, and band shifts, suggest heterogeneity of the Lewis acidic sites on TiO_2 . Although weak Brønsted acidity has been reported following adsorption of trimethylamine,¹⁸ these Brønsted acid sites are not of adequate strength to protonate pyridine and thus, as expected, TiO_2 does not exhibit Brønsted acidity in the presence of quinoline.

Adsorption on ZrO_2 . The existence of Brønsted acid sites on ZrO_2 has been reported by Hertl¹⁹ in an IR spectroscopic investigation of NH_3 and pyridine adsorption. This is controversial since the amount of residual strongly adsorbed water decreased and thus formation of NH_4^+ may be due to protonation of the base by water. In the present study, it was found that the IR spectra of quinoline adsorbed on ZrO_2 closely resemble the spectra obtained following adsorption of quinoline on TiO_2 , indicating that the pure oxide surfaces are predominantly of Lewis acidic nature. At low surface coverage, band positions indicate quinoline to be involved in both hydrogen bonding and Lewis acid interactions. Further adsorption results in the growth of a band at 1598 cm^{-1} at the expense of the band at 1588 cm^{-1} . After prolonged evacuation, the

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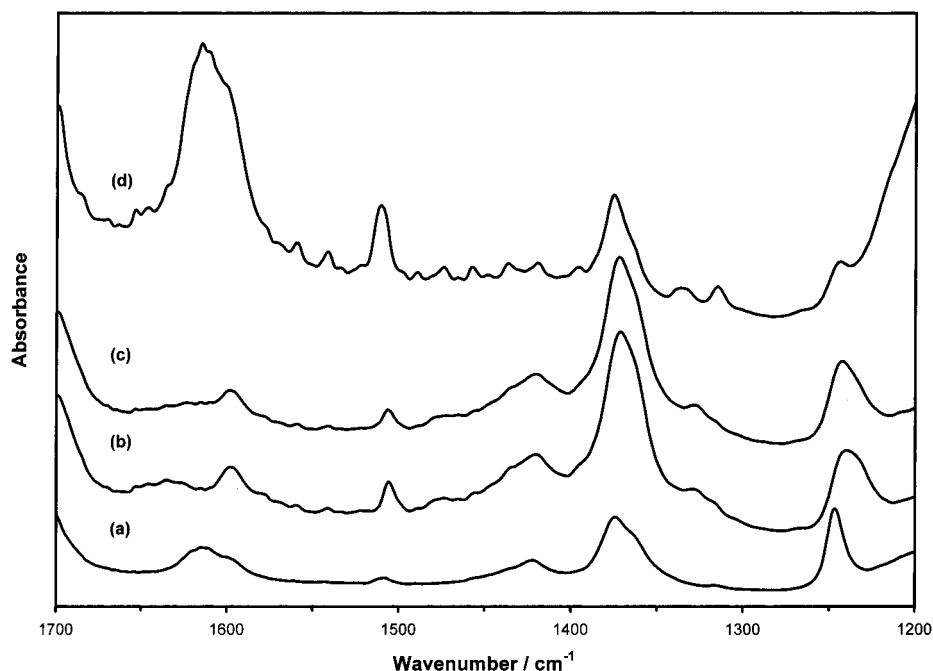


Figure 8. IR spectra of quinoline on sepiolite at increasing coverage (a) to (c) and following evacuation at room temperature overnight (d).

1588 cm^{-1} band does not reappear but a weak shoulder appears at 1582 cm^{-1} . A possible explanation may involve the consideration that the 1588 cm^{-1} band is due to a hydrogen-bonded species. The broadness of this band may mask the weaker band at 1582 cm^{-1} , which could possibly be due to a chemisorbed species. In the lower spectral region, the bands are generally broader and not well resolved, suggesting that hydrogen-bonded species are still present at the surface although the spectrum in the $\nu(\text{OH})$ region is not of sufficient quality to allow confirmation of this. The strong band at 1362 cm^{-1} shifts to 1371 cm^{-1} and decreases in intensity following prolonged evacuation. This behavior more closely parallels the corresponding band observed for quinoline on SiO_2 than on TiO_2 and may infer that Lewis acid sites on ZrO_2 are weaker than those on TiO_2 . Confirmation of weaker Lewis acid sites on ZrO_2 is provided by the shift of the ring-breathing vibration, since ring-breathing modes are known to be sensitive to the strength of the interaction of the lone pairs.

Adsorption on Niobic Acid. The IR spectrum of quinoline adsorbed on niobic acid provides evidence for quinoline being involved in three modes of interaction with the niobic acid surface. The broadness of some bands can be accounted for by hydrogen-bonded species, which is expected in view of the calcination temperature (100 $^{\circ}\text{C}$). Following evacuation, a number of bands become better resolved, especially in the 1600 cm^{-1} region where a band emerges at 1601 cm^{-1} and is assigned to a ring-stretching vibration of the quinolinium ion. Bands at 1559, 1439, 1396, and 1307 cm^{-1} are also attributed to ring vibrations of the quinolinium ion. The remaining bands observed after prolonged evacuation are assigned to ring vibrations of chemisorbed quinoline species. Band positions indicate that the concentrations of Brønsted and Lewis acid sites on niobic acid are comparable and that the concentrations of both species are comparable with those found on the $\text{SiO}_2\text{-Al}_2\text{O}_3$ surface. However, the concentration of Brønsted acid sites with $\text{p}K_a < 4.9$ is less on the niobic acid surface than on *H*-mordenite.

Adsorption on $\text{SiO}_2\text{-Al}_2\text{O}_3$ and *H*-Mordenite. The IR spectra of quinoline adsorbed on $\text{SiO}_2\text{-Al}_2\text{O}_3$ provide

evidence that the oxide surface is functioning both as an electron acceptor and a proton donor. With increasing surface coverage, the spectra become noisy, especially around the 1600 cm^{-1} region and between 1500 and 1400 cm^{-1} , attributed to the formation of hydrogen-bonded species and possibly physisorbed quinoline. On evacuation, the bands arising from the ligation of quinoline to Lewis acid sites either increase or decrease in intensity, indicative of the heterogeneity of the Lewis acidic centers on the $\text{SiO}_2\text{-Al}_2\text{O}_3$ surface. The spectrum obtained following overnight evacuation provides evidence that quinoline is adsorbed on strong Lewis acid sites and Brønsted acid sites with $\text{p}K_a < 4.9$.

Adsorption of quinoline on *H*-mordenite also leads to formation of the quinolinium ion and coordinated quinoline. The spectral data provide evidence for a larger concentration of Brønsted acid sites with adequate strength, and accessible to quinoline, compared with $\text{SiO}_2\text{-Al}_2\text{O}_3$. However, there is a smaller number of bands due to adsorption on Lewis acid sites on *H*-mordenite. It is probable that a greater proportion of Lewis acidic sites are concentrated in zeolite pores which are more sterically restrictive to quinoline molecules. The IR spectrum is well-resolved, all bands become sharper during evacuation, and the bands ascribable to quinoline adsorption on Lewis acid sites are removed on evacuation. Basila and Kantner²⁰ have reported that the introduction of water to $\text{SiO}_2\text{-Al}_2\text{O}_3$ with adsorbed pyridine resulted in the conversion of Lewis acid sites to Brønsted acidic sites. In the present study, it was not possible for the surface to become contaminated with H_2O during evacuation, and a possible explanation for the removal of the bands attributed to interaction with Lewis acid sites is that the electron deficient aluminum atoms acting as Lewis acid sites are weaker on *H*-mordenite than on the $\text{SiO}_2\text{-Al}_2\text{O}_3$ surface.

Adsorption on Sepiolite. Sepiolite is a clay mineral which is a fibrous magnesium silicate of ideal formula $[\text{Si}_{12}\text{Mg}_8\text{O}_{30}(\text{OH})_4](\text{H}_2\text{O})_4 \cdot 8\text{H}_2\text{O}$.²¹ There are channels of

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Table 3. Summary of Conclusions Based on Adsorption of Quinoline on Oxides

SiO ₂	Weakest H-bond interaction.
TiO ₂	H bonding and Lewis interaction. Stronger H bonding than on silica.
ZrO ₂	Evidence that Zr ⁴⁺ are weaker than Ti ⁴⁺ .
niobic acid	Concentration of both types of acid sites comparable with SiO ₂ -Al ₂ O ₃ .
SiO ₂ -Al ₂ O ₃	Three modes of interaction identifiable. Brønsted acid sites with pK _a <4.9.
H-mordenite	Larger concentration of Brønsted acid sites than on SiO ₂ -Al ₂ O ₃ .
	Smaller concentration of Lewis acid sites. Possibly diffusion limited.
sepiolite	Lewis and H-bonding interactions. Not diffusion limited.

dimensions 5.6×11 Å along which there are protons, coordinated water, and exchangeable cations. Sepiolite is reported to be weakly acidic.²² The open channels of the corrugated sepiolite surface should have sufficient capacity to accommodate quinoline molecules. The IR spectrum of the sepiolite calcined at 400 °C displays bands in the $\nu(\text{OH})$ region at 3723, 3671, 3605, and 3530 cm⁻¹, although Cannings²³ has reported bands at 3740, 3674, 3599, and 3532 cm⁻¹ for sepiolite sample calcined at 400 °C. On adsorption of quinoline, the band due to the silanol group at 3723 cm⁻¹ is shifted to 3715 cm⁻¹, ascribed to a hydrogen bonding, although the other bands in this region do not appear to be affected by quinoline adsorption. The IR spectra in the quinoline ring vibration region display bands at 1615, 1508, 1422, 1374, and 1247 cm⁻¹. The broad band at 1615 cm⁻¹, due to the deformation mode of water, clearly demonstrates the existence of water in the channels after calcination at 400 °C in agreement with Cannings.²³ The bands at 1508 and 1374 cm⁻¹ are ascribed to quinoline interacting with Lewis acid sites, and the band at 1422 cm⁻¹ is ascribed to a hydrogen-bonded species. The 1247 cm⁻¹ band could be attributable to a Si-O-Si vibration, a band in the 1200 cm⁻¹ region has been reported to indicate the existence of Si-O-Si in a near linear configuration.²⁴ However, Si-O-Si vibrations are generally found at a lower wavenumber and this assignment may not be correct. It is possible that the sepiolite sample may contain a mineral impurity which is responsible for this band. An alternative assignment could be to hydroxyl group deformation. Although a band in this region is not reported in the literature, it is apparent that, with increasing coverage, the 1615 cm⁻¹ band disappears, indicating the displacement of adsorbed water by quinoline. These observations provide evidence for the adsorption of quinoline inside the sepiolite channels. However, the bands at 3605 and 3530 cm⁻¹, ascribed to the antisymmetric and symmetric stretching modes of adsorbed water, remain unaffected by quinoline adsorption.

These bands are believed to be associated with strongly held structural water molecules. Evacuation causes the removal of the hydrogen-bonded species, as evidenced by the disappearance of the 1422 cm⁻¹ band and the shift of the 3715 cm⁻¹ band back to its original position. Furthermore, the band due to the water deformation mode (1615 cm⁻¹) is restored, indicating that the molecules are not strongly held in the channels. The bands ascribed to the interaction with Lewis acid sites remain after prolonged evacuation.

General Conclusions

The behavior of quinoline adsorbed on oxide surfaces is summarized in Table 3. The IR spectra of quinoline adsorbed on SiO₂, TiO₂, ZrO₂, and sepiolite show that adsorbed molecules are either coordinated to Lewis acidic centers or involved in hydrogen-bonding interactions. The protonic surface acidity of these oxides is insufficiently strong to enable them to function as Brønsted acids in the presence of quinoline. Protonation only occurs on niobic acid, SiO₂-Al₂O₃, and H-mordenite, indicating that these oxide surfaces exhibit Brønsted acidic sites with pK_a values ≤ 4.9 . These results are complementary to those obtained using NH₃ or pyridine as probe molecules, whose conjugate acids have pK_a values of 9.25 and 5.25, respectively. The application of heterocyclic nitrogen bases other than pyridine, such as quinoline, therefore enables a study of stronger acidic sites and the ability to differentiate these from the weaker ones. In a recent study, we have reported the adsorption of diazines on several oxide surfaces²⁵—these are molecules which are only protonated at much stronger acidic sites. Thus, by measurement of the IR spectra of a selection of suitable probe molecules, it will become possible to assess a wide range of strengths of Brønsted acidic sites on oxide surfaces, that is, information that is crucial to the understanding of their catalytic behavior.

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