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# The retention of heterocyclics by siliceous frameworks

## Part I *The role of the heterocyclic*

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Flow microcalorimetry has been used to probe acid-base interactions between five-membered-ring heterocyclics and thermally pre-treated, porous silica. The adsorbates (1-methylpyrrolidin-2-one, pyridine, pyrrolidine, pyrrole, 2-methylthiophene, 2-octyl-4-isothiazolin-3-one, 4,5-dichloro-2-octyl-4-isothiazolin-3-one and 2-cyclopentenone,) varied in basicity, polarity and $\pi$-character. The amounts of the adsorbates retained by the silica were determined, along with enthalpy of adsorption (ranging from $-5.5$ kJ mol$^{-1}$ to $-57.8$ kJ mol$^{-1}$) and enthalpy of desorption (ranging from 5.6 kJ mol$^{-1}$ to 26.1 kJ mol$^{-1}$). For the majority of the adsorbates the enthalpy of adsorption is consistent with hydrogen bonding to isolated silanols. Although increasing basicity enhanced the adsorption enthalpy and hence the strength of associations, desorption was inhibited when a carbonyl, or unsaturated carbonyl, group was adjacent to the active basic centre. Bulky electron-withdrawing agents (chlorine atoms) substituted at the double bond of the unsaturated carbonyl reduced the adsorption considerably. This was attributed to steric hinderance restricting the proximity of the basic groups with the active silanol sites.

## 1. Introduction

The ability of siliceous materials to participate in adsorption, adhesion and catalysis is facilitated by their surface geometry and bulk porosity. Broadly speaking silica is considered to be a polymer of silicic acid consisting of inter-linked $SiO_4$ tetraheda. This construction terminates by the formation of siloxane bridges (Si-O-Si) or silanol groups (SiOH). The surface chemistry of silica is dominated by the nature, distribution and accessibility of these structures [1].

Since Kislev [2] discovered hydroxyl groups on the surface of silica, numerous studies on the assignment of different hydroxyl types have been published. From these studies silanol sites may be distinguished as: isolated (single or free) silanols; vicinal (or bridged) silanols, which are characterised by their ability to hydrogen bond; and geminal silanols, which consist of two hydroxyls attached to the same silicon atom and as such are too close to mutually hydrogen bond (Scheme 1). These groups may be further classified as: Single silanols surrounded by other single silanols ($S_m$); single silanols on an edge ($S_e$); single silanols ($S_p$) perturbed by hydrogen bonding with a neighbouring geminal hydroxyl at a step ($G_p$); and geminal silanols at an edge ($G_e$) (Scheme 2). The existence of geminal silanols has been the subject of some debate, but if their presence is accepted then their contribution to the total silanol number is considered to be relatively small. Numerous workers have concluded that the number of silanol groups per nm$^2$ of a silica surface (the silanol number, $\alpha_{OH}$) is a constant independent of the type of silica. Siloxane sites may also be differentiated as: $(\text{-SiO-})_2$, $(\text{-SiO-})_3$, $(\text{-SiO-})_5$, or $(\text{-SiO-})_6$ rings.

When silica is heated its surface dehydrates [3–5]. At 100°C physisorbed water is removed, such that when a temperature of 200°C is achieved only silanol groups and siloxane bridges remain. Between 400 and 600°C vicinal silanols condense to leave isolated, geminal and terminal silanols; along with strained siloxane bridges. Between 600 and 800°C the internal silanols condense and by 1000°C only isolated silanols remain. It necessarily follows that during this process the distance between a silanol site and its next near neighbour increases. This chemistry can be used to control the availability of specific sites for adsorption.

The adsorption of covalent species onto the silica surface has been studied extensively. Curtoys *et al.* [6] classified molecules into three groups, according to the strength of their interaction (low, medium, strong) with the silica surface. Those with low interaction include nitrogen, carbon tetrachloride, *n*-hexane, cyclohexane; those with medium interaction encompass diethyl ether,

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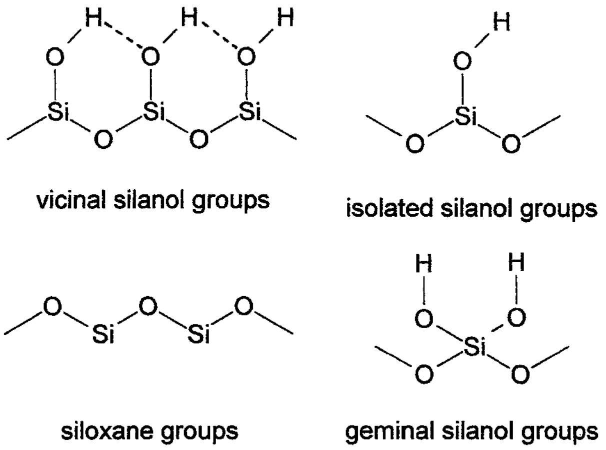
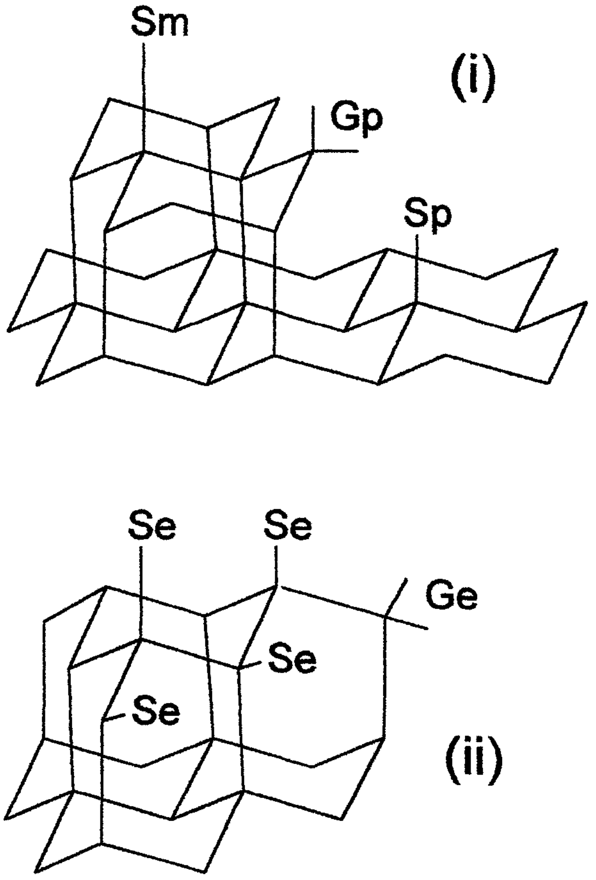
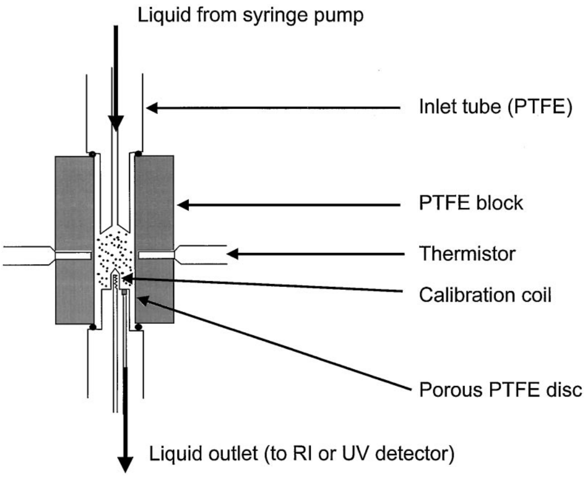


*Scheme 1* Types of hydroxyl (silanol) groups on the surface of amorphous silica.



*Scheme 2* Distinction of silanol sites, using the {111} planes of $\beta$-cristabolite as a model, at steps (i) and edges (ii) on the silica surface.

benzene, acetone, tetrahydrofuran; while pyridine and triethylamine are typical of molecules exhibiting strong interactions. Although it has been universally demonstrated that the strength of interaction is related to polarity of the adsorbate the relationship is not a simple one and the electron accepting or donating character (acid-base properties) are clearly important. By definition silanol groups are weakly acidic, but the variation in Si-O bond angles leads to a spectrum of activities. Despite the prolific literature an unambiguous means to quantify the acidity of specific adsorption sites has remained elusive.



*Scheme 3* Diagram of a typical Flow Microcalorimeter (FMC).

There has been much interest of late in the development of theoretical models expressing the acidity and basicity of interacting species in terms of their enthalpy of association. The method of Flow Microcalorimetry (FMC) has been used to study the association of particulate inorganic materials, such as silica, with probes having known acid-base characteristics. The FMC technique was designed to measure the heat exchanged as result of adsorption/desorption phenomena occurring under flow conditions (Scheme 3) [7]. A differential refractometer, downstream to the calorimeter allows quantification of an adsorbate. The amount of solute adsorbed on the solid is calculated from the comparison of parallel experiments conducted with the solid and a non-adsorbing probe. The difference between the refractometer signals of the two experiments permits the calculation of the amount of adsorption. Appropriate calibration also allows an indirect measurement of the enthalpies associated with adsorption and desorption.

Using this technique it is possible to adapt the model proposed by Drago [8, 9] to quantify the covalent and electrostatic contributions governing adsorption, according to:

$$-\Delta H_{\mathrm{AB}} = C_{\mathrm{A}} C_{\mathrm{B}} + E_{\mathrm{A}} E_{\mathrm{B}}$$

Where $\Delta H_{\mathrm{AB}}$ is the adsoption enthalpy associated with an acidic species A, and a basic species B. $C_{\mathrm{A}}$ and $C_{\mathrm{B}}$ are the covalent constants and $E_{\mathrm{A}}$ and $E_{\mathrm{B}}$ are the electrostatic constants for the acid and base. For silica of undisclosed source the electrostatic and covalent constants for the acid silanol sites have been quoted as 4.4 and 1.1, using data derived from the adsorptions of triethylamine, pyridine and ethylacetate. Unfortunately Drago's approach is limited by the assumption that the associated species must be purely acidic or basic, and because of this the FMC method has been the subject of criticism. However, there is at least some qualitative agreement with more sophisticated methods of determining acid-base interactions.

With this in mind the current series of papers employ FMC along with diffuse reflectance infrared spectroscopy (DRIFTS) to examine the interaction of a range of heterocyclics with porous silicas. The heterocyclics were selected to mirror common structural features of isothiazolinones. Isothiazolinones are active biocides and the interest here, in addition to assessing the value of the FMC technique, was to identify whether porous silicas might be used to control their release to a given environment [10]. In an effort to understand how the nature and distribution of surface sites dictate optimum adsorption, the silicas were thermally pre-treated to deliberately and systematically alter their chemistry.

## 2. Experimental

### 2.1. Materials

The silica used in this study was prepared by Crosfield Ltd. The sample was calcined using a Carbalite Rotary Calciner at 700°C for 1 hour, and had a B.E.T. surface area of 552 $m^2$ $g^{-1}$, average pore diameter (APD) of 25 Å and average particle size ($d_{50}$) of 4.3 $\mu$m. The adsorbates used in this study were all HPLC grade, supplied by Aldrich Chemicals, with the exception of the isothiazolinones, which were supplied by Thor Specialities, U.K.

### 2.2. Flow microcalorimetry (FMC)

The FMC system used consisted of a Microscal© 3V FMC, with a PTFE fluid path upgrade, linked to a Waters® 410 differential refractometer. Data was output to a Perkin-Elmer© Nelson 900 series data station with appropriate software. Experiments were conducted using a cell temperature of 28 °C ± 0.5 °C and adsorbate concentrations of 0.3% w/v. Decahydronaphthalene was used as the non-adsorbing probe, and cyclohexane (HPLC grade dried over 4 Å molecular sieve) as the solvent for the isothiazolinones. The flow rates for both the non-adsorbing probe and the solvent were 3.30 $cm^3$ $h^{-1}$. Within the FMC cell the adsorbent (volume 0.15 $cm^3$; 350–800 mg) was equilibrated, with cyclohexane, for 18 hours before measurements commenced. This conditioning period was necessary to remove the vast majority of loosely bound surface water from the silica substrate. Initially the adsorbate in cyclohexane was passed through the cell containing the siliceous adsorbent, and after adsorption had taken place cyclohexane was passed through the cell to facilitate desorption. For both adsorption and desorption measurements, data reported is that for the average result between two runs, such that the spread of the data is less than ±5%.

### 2.3. Infrared spectroscopy

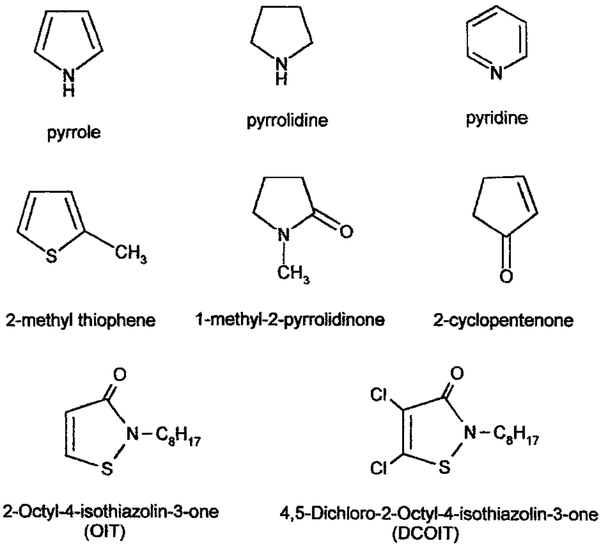
After the FMC adsorption experiment, the silica powders were removed from the fMC cell and blended with KBr (5% w/w). DRIFTS spectra were obtained in the range 4000–500 $cm^{-1}$, at a resolution of 4 $cm^{-1}$ from an average of 150 scans. The instrument used was a Nicolet 510P FTIR, using a DTGS detector, and fitted with a Spectra-Tech DRIFTS cell.

## 3. Results and discussion

This study is divided into three parts. In Part I we consider how the functionality of the adsorbate influences the strength of surface interactions. To facilitate this silica of specified surface area, porosity and surface character (Table I) was selected to act as the adsorbent, while various heterocyclics were chosen as adsorbates. The heterocylics were selected to cover a range of basicities, dipole moments and $\pi$-character (Scheme 4). FMC was employed to determine enthalpies of adsorption, desorption, and the amounts of biocides retained by silica. DRIFTS was adopted to clarify the nature of structural interactions.

TABLE I pH, porosymmetry and particle size data of the amorphous silica adsorbent

| pH | B.E.T. surface area ($m^2$ $g^{-1}$) | Pore volume (ml $g^{-1}$) | Average pore diameter (Å) | Average particle size ($\mu$m) $d_{50}$ | Cumulative Pore Area (BJH) (20–50 Å) ($m^2$ $g^{-1}$) | $\alpha_{OH}$/$nm^2$ (±0.3) |
|---|---|---|---|---|---|---|
| 4.4 | 552 | 0.34 | 25 | 4.3 | 321 | 1.87 |



*Scheme 4* Structures of the adsorbates used in the FMC and DRIFTS studies.

According to the literature, the adsorption of polar molecules onto siliceous substrates is associated with non-hydrogen bonded silanol groups. Here the adsorption of species such as diethylamine and ammonia is believed to be stoichiometric [11]. The silica used in this study has been heated to remove hydrogen bonded silanol groups, to assist a stoichiometric reaction of the heterocyclics with the available silanol sites. Furthermore, the adsorption activity from non-aqueous media (the solvent used in this study is cyclohexane) has been attributed to Lewis acid-base interactions. Physical data for the heterocyclic probes is listed in Table II with accompanying p$K_a$ values and relative basicities, where available. The relative basicity ($H_B$) is defined as the p$K_a$ + 1.74 [12].

Figs 1 and 2 show the enthalpies of interaction (adsorption and desorption respectively) for the heterocyclics with the silica framework. The enthalpies of adsorption range from −5.5 kJ $mol^{-1}$ to −54 kJ $mol^{-1}$. The rather weak interactions for 2-methylthiophene (−5.5 kJ $mol^{-1}$) and pyrrole (−16.9 kJ $mol^{-1}$) are

TABLE II Physical data for the adsorbents used in the FMC study

| Adsorbate | Dipole moments ($\mu$/D) | Dielectric constant ($\varepsilon$) | p$K_a$ | Relative basicity |
|---|---|---|---|---|
| 2-methyl thiophene | 0.674 | 2.739<br>(thiophene) | | |
| Piperidine | 1.19 | 4.33 | | |
| Pyrrole | 1.74 | 8.0 | 0.4 | 2.14 |
| Pyrrolidine | – | 8.3 | 11.27 | 13.01 |
| Pyridine | 2.215 | 13.26 | 5.25 | 6.99 |
| 2-cyclopentanone | 3.3 | 13.58 | | |
| N-methyl pyrrolidin-2-one | | 32.55 | | |

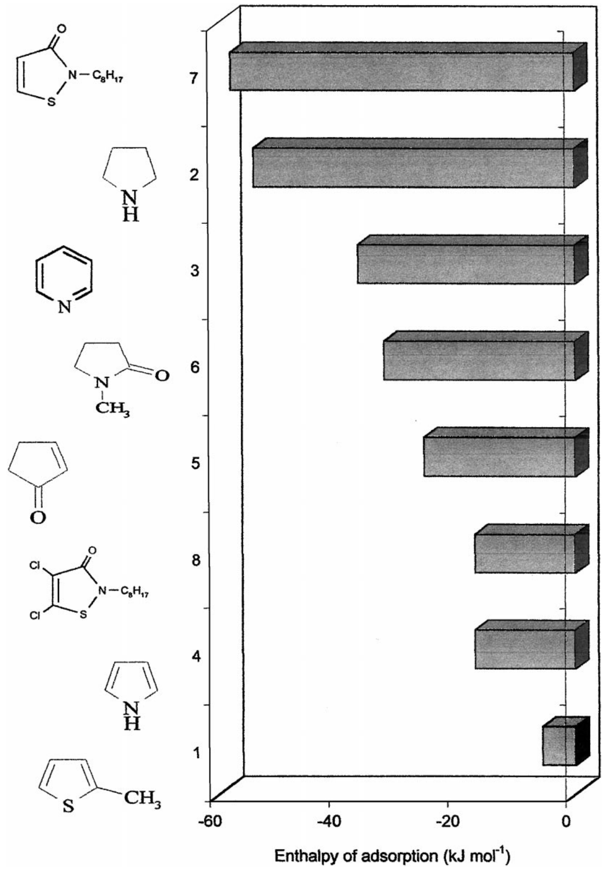


*Figure 1* Enthalpies of adsorption (kJ mol$^{-1}$) for the heterocyclics: 2-methylthiophene (1), pyrrole (4), DCOIT (8), cyclopenten-2-one (5), 1-methylpyrrolidin-2-one (6), pyridine (3), pyrrolidine (2) and OIT (7); on a silica of surface area 552 m$^2$ g$^{-1}$, calcined for 1 hour at 700°C.

consistent with a physisorption process; this encompassing short-range negative attractions arising from van der Waals forces, with a contribution from permanent dipoles. The magnitude of the two enthalpies may reflect the fact that both molecules are $\pi$-excessive heterocyles, in which the dipole vector is directed *away* from the heteroatom. Aromatic molecules tend to interact readily with silanol groups, through the donation of $\pi$-electrons. However, in pyrrole the sp$^2$-hybridized nitrogen bears a hydrogen substituent in the plane of the molecule, whereas in thiophene the second electron lone pair of sulphur is placed into one of the sp$^2$ hybrid orbitals, again in the plane and thus with no opportunity to achieve overlap. It is unlikely that this electron pair is able to act as an efficient nucleophile, since the methyl group in 2-position of the ring may sterically hinder any interaction with silanol groups. For pyrrole to function as a base it must lose its aromatic character, and as such it is a very weak base (p$K_a = 0.4$) (Table II). On this basis it is likely that pyrrole will interact only with the more acidic of the silanol groups.

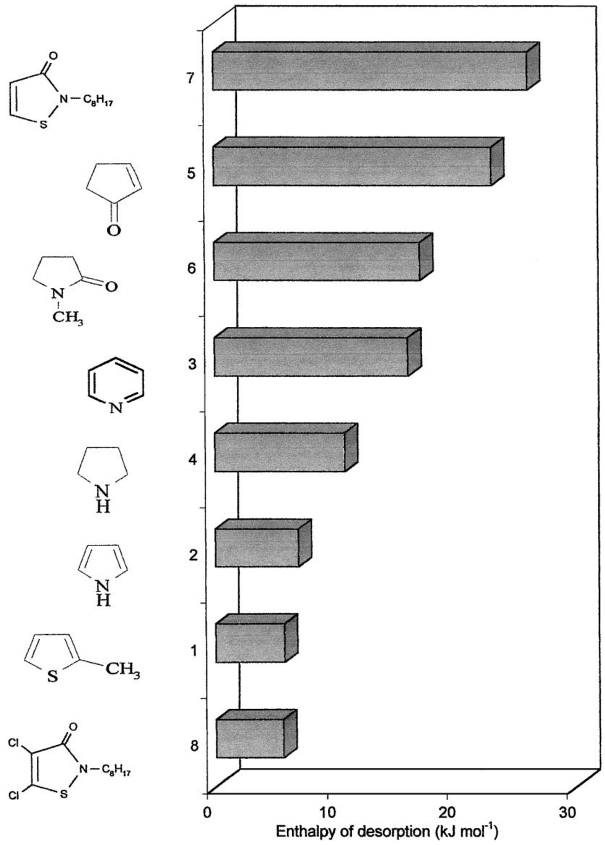


*Figure 2* Enthalpies of desorption (kJ mol$^{-1}$) for the heterocyclics: DCOIT (8), 2-methylthiophene (1), pyrrole (2), cyclopenten-2-one (5), 1-methylpyrrolidin-2-one (6), pyridine (3), pyrrolidine (4) and OIT (7); on a silica of surface area 552 m$^2$ g$^{-1}$, calcined for 1 hour at 700°C.

In contrast, the adsorption enthalpies of pyridine and pyrrolidine were $-37$ kJ mol$^{-1}$ and $-54$ kJ mol$^{-1}$ respectively, consistent with strong hydrogen bonds between the heterocycles and silanol groups. These values concur with those in the literature. According to Proctor [13] there is a strong hydrogen bond between pyridine and silica, the activation energy of desorption being $43.6 \pm 4.2$ kJ mol$^{-1}$, which is similar to the heat of adsorption of $-45.2 \pm 3$ kJ mol$^{-1}$ obtained by Hertl and Hair [14]. Consistent with this trend, the adsorption enthalpy for piperidine ($-44$ kJ mol$^{-1}$) lies between these two values. Like piperidine and pyrrolidine the dipole vector of pyridine is directed *towards* the heteroatom, and hence pyridine is a $\pi$-deficient heterocycle. However, the dipole moment of pyridine is larger than pyrrolidine because the nitrogen is sp$^2$ hybridized, meaning that it is less polarisable. Because of these structural characteristics, both pyridine and pyrrolidine are more basic than pyrrole, having p$K_a$s of 5.25 and 11.27 respectively (Table I). The net effect is that both pyridine and pyrrolidine have an available electron pair on the nitrogen and can thus be protonated or interact with electrophiles, hence their substantial adsorption activity.

That the interaction was not simply related to the basicity of the adsorbate was demonstrated by the adsorption (desorption) enthalpies associated with

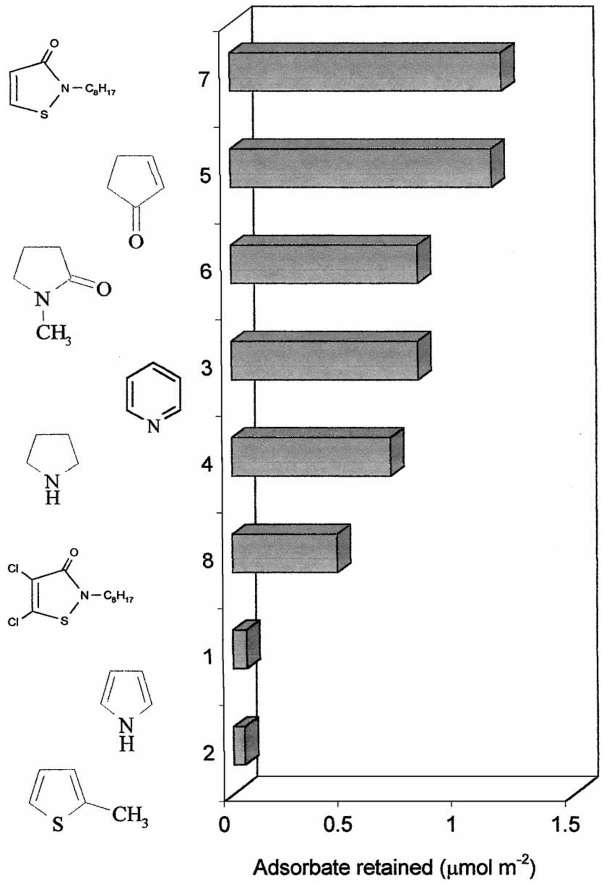


*Figure 3* Adsorbate retained ($\mu$mol m$^{-2}$) on a silica of surface area 552 m$^2$ g$^{-1}$, calcined for 1 hour at 700°C; for the heterocyclics: 2-methylthiophene (2), pyrrole (1), DCOIT (8), cyclopenten-2-one (5), 1-methylpyrrolidin-2-one (6), pyridine (3), pyrrolidine (4), and OIT (7).

2-cyclopentenone and 1-methylpyrrolidin-2-one. For 2-cyclopentenone the enthalpy of $-25.4$ kJ mol$^{-1}$ was consistent with that expected for hydrogen bonding of the unsaturated carbonyl with silanol groups. Although 1-methylpyrrolidin-2-one had a slightly higher enthalpy of $-32.2$ kJ mol$^{-1}$ the desorption enthalpy and amount of this adsorbate retained by the silica was less than that for 2-cyclopentenone (Fig. 3). In fact on comparing Figs 1–3, it can be seen that the trend in the amount of adsorbate retained by the silica (Fig. 3) matched the trend in enthalpy of desorption (Fig. 2), such that 2-cyclopentenone $>$ 1-methylpyrrolidin-2-one $>$ pyridine $>$ pyrrolidine $>$ pyrrole $>$ 2-methylthiophene. However, the trend in adsorption activity was somewhat different: Here the order was: pyrrolidine $>$ pyridine $>$ 1-methylpyrrolidin-2-one $>$ 2-cyclopentenone $>$ pyrrole $>$ 2-methylthiophene. From this it might be inferred that the acid-base interaction of the silanol groups with the adsorbate is the stronger. However, it is possible that once the molecule is adsorbed some conformational stability may be afforded when an unsaturated carbonyl group is present, or when a nitrogen atom is neighbour to a carbonyl group in the heterocyclic ring.

The differences in adsorption-desorption activity are better understood by examining two isothiazolinone structures: 2-Octyl-4-isothiazolin-3-one (OIT) and 4,5-Dichloro-2-octyl-4-isothiazolin-3-one (DCOIT). The OIT exhibits the largest adsorption enthalpy of all the molecules examined, whilst the DCOIT accounts for one of the smallest. For DCOIT the adsorption enthalpy is reduced by a factor of 3.4, mirroring that of 2-methyl thiophene and pyrrole. Here *two* features of the isothiazolinone structure dictate adsorption activity, the cyclic amide and the conjugated carbonyl. The amide group is able to tautomerize and as such this process would certainly enhance the strength of any interaction with silanol groups. The relative import of withdrawing electron density away from this conjugated structure is seen for the DCOIT.

If we consider the adsorbates collectively then optimum adsorption activity could be explained by the ability to form hydrogen bonds to silanol sites. Hydrogen bonds can be formed between donor and acceptor groups when the molecular configuration and conformation brings them within hydrogen bond geometry. When the A$-$(H)$\cdots$B distance is very short i.e. (H)$\cdots\cdot$B $<$2.5 Å, a strong hydrogen bond is formed. When the distance is between 2.5 and 3.2 Å, normal hydrogen bond may be formed. On this basis the relatively low adsorption activity of DCOIT might be explained in terms of steric hindrance, brought about by the two chloro-substituents restricting the angle of approach and hence distance of the amide from silanol groups.

To further rationalize the interactions of the heterocyclics with the silica it is appropriate at this stage to examine the nature of active silanol sites. In this respect vibrational spectroscopy is useful. Accordingly, DRIFTS spectra of the silica samples recovered from the FMC cell following adsorption were recorded.

A band centred at 3740 cm$^{-1}$, and a broad tail characterizes the vibrational spectrum of the silica surface. This band is universally attributed to isolated (SiOH) and geminal (Si(OH)$_2$) silanol groups. Depending on the specific study, a shoulder at 3720 cm$^{-1}$ has been attributed to either geminal or terminal silanol groups [15]. This spectrum is characteristic up to 150°C, but above (200–600°C) several changes ensue. The band at 3720 cm$^{-1}$ is very much reduced in intensity and the peak at 3740 cm$^{-1}$ is enhanced, shifting slightly to 3748 cm$^{-1}$. Because the silica used in this study has been thermally pre-treated the latter band is more characteristic of the spectra presented here. Other regions of interest are listed in Table III, and the data is discussed with reference to these assignments.

TABLE III Assignment of infrared bands in the spectrum of porous silica

| Wavenumber (cm$^{-1}$) | Assignment |
|---|---|
| 3746 | Isolated OH stretch |
| 3742 | Geminal OH stretch |
| 3730–3720 | Hydrogen perturbed vicinal OH |
| 3650 | Intraglobular OH |
| 3520 | Oxygen perturbed vicinal OH |
| 3500–3400 | Adsorbed $H_2O$ |
| 1625 | $H_2O$, OH bending $H_2O$ |
| 1250–1020 | Asymmetric Si-O-Si stretch |
| 970 | Si-O-(H- - -$H_2O$) |
| 870 | SiOH, OH bending |
| 800 | Geminal SiOH in-plane bending |
| 600 | Geminal SiOH in-plane bending |

## 3.1. 3800–2800 cm$^{-1}$

All the spectra showed a peak at 3748 cm$^{-1}$ in this region, characteristic of isolated and geminal silanol groups (Figs 4–7). Any broadening and shift of this peak is consistent with association of silanol groups with the heterocyclic. Both 2-methyl thiophene and pyrrole showed insubstantial changes to this band, supporting the previous observations from FMC that only a minimal number of these molecules interact with the silica (Fig. 4). For 1-methyl-2-pyrrolidinone and 2-cyclopentenone the intensity of the 3748 cm$^{-1}$ absorption was reduced by almost one half, but there was no shift in the position of the absorption (Fig. 6). By comparison, pyrrolidine showed a significant reduction in the intensity of this band, coupled with a broadening and frequency shift of its maximum, supporting the earlier premise that this molecule adsorbs strongly to isolated silanol sites (Fig. 5). This was also seen, albeit to a lesser extent, for pyridine. The absorptions associated with OIT and DCOIT confirm these trends (Fig. 7). The intensity of the 3748 cm$^{-1}$ peak is reduced to the greatest extent for OIT, while DCOIT shows changes more characteristic of 2-methyl thiophene and pyrrole.

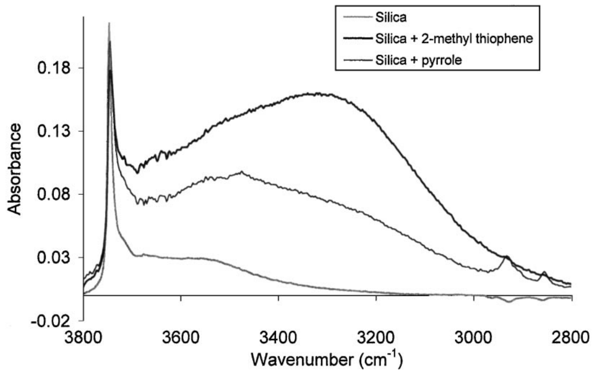


*Figure 4* Infrared spectra of silica in the range 3800–2800 cm$^{-1}$, showing the adsorption of 2-methylthiophene and pyrrole.

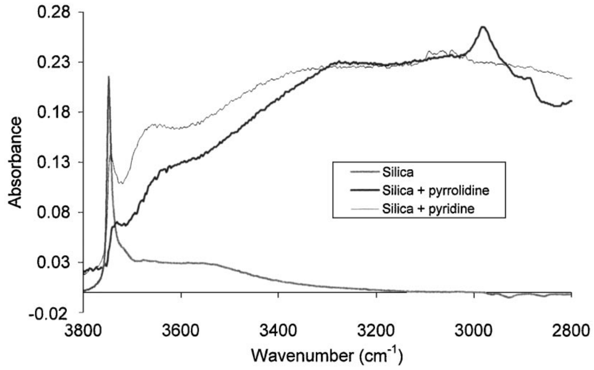


*Figure 5* Infrared spectra of silica in the range 3800–2800 cm$^{-1}$, showing the adsorption of pyrrolidine and pyridine.

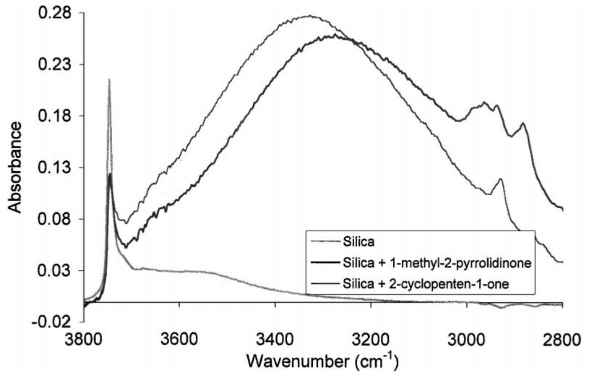


*Figure 6* Infrared spectra of silica in the range 3800–2800 cm$^{-1}$, showing the adsorption of 1-methyl-2-pyrrolidinone and 2-cyclopenten-1-one.

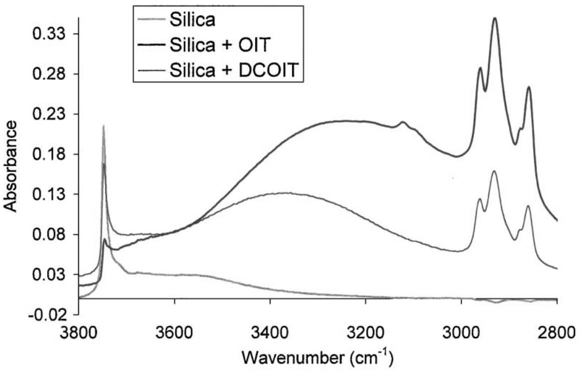


*Figure 7* Infrared spectra of silica in the range 3800–2800 cm$^{-1}$, showing the adsorption of OIT and DCOIT.

## 3.2. 1750–1550 cm$^{-1}$

This region was of particular value when examining the interactions of the molecules containing carbonyl groups with the silica surface. Fig. 8 depicts these

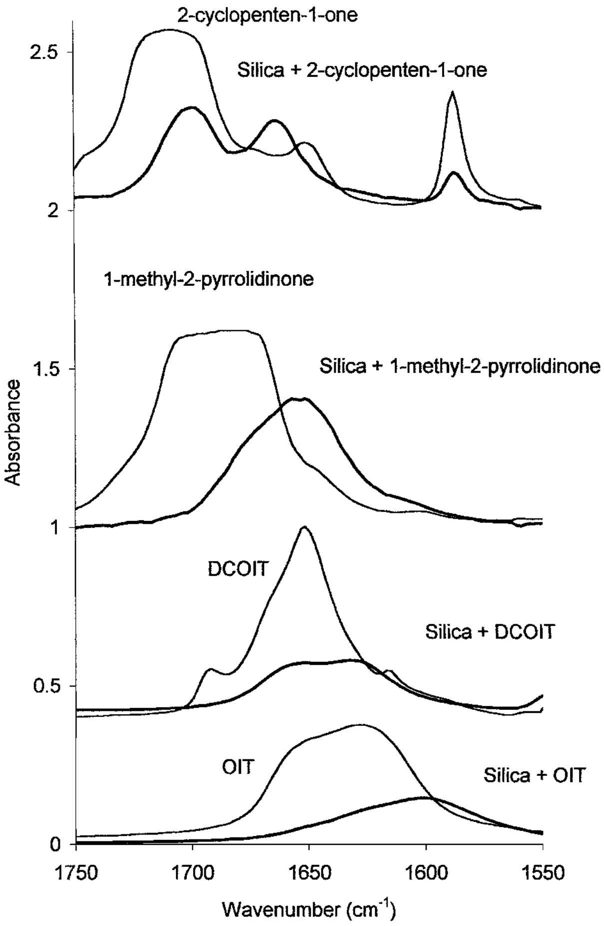


*Figure 8* Infrared spectra of OIT, DCOIT, 1-methylpyrrolidin-2-one and 2-cyclopenten-1-one, and their counterparts adsorbed on silica in the region 1750–1550 cm$^{-1}$.

changes for OIT, DCOIT, 1-methyl pyrrolidin-2-one and 2-cyclopentenone. The largest shifts in the carbonyl band are seen for OIT and 1-methyl-2-pyrrolidinone. The magnitude of the band shifts further supports the premise that hydrogen bonding exists between silanols and the carbonyl group. Where such interactions exist the fundamental absorption shifts to lower frequency by 5–50 $\text{cm}^{-1}$ with accompanying reduction in intensity and band broadening. In contrast the shift is relatively insignificant for DCOIT, suggesting that any association is rather weak. The most informative changes are seen for 2-cyclopentenone. For this conjugated carbonyl two absorptions are characteristic, that near 1700 $\text{cm}^{-1}$ due to the unsaturated carbonyl and that near 1650 $\text{cm}^{-1}$ due to the carbonyl conjugated alkene. On adsorption to the silica the unsaturated carbonyl shifts to lower frequency suggesting that it has associated with silanol groups, the magnitude of this shift suggesting hydrogen bonding. In contrast the alkene absorption shifts to higher frequency, suggesting that conjugation with the carbonyl has been weakened, supporting the premise that it is the carbonyl group rather than the alkene that associates with the silica surface.

## 3.3. 1200–1020 $\text{cm}^{-1}$

This region gives information on the Si-O-Si asymmetric stretching vibrations of the silica surface. Although not depicted here, there were no obvious changes to the spectra in this region, confirming that it is the silanol sites rather than the siloxane bridges, which participate in adsorption.

## 3.4. 1000–500 $\text{cm}^{-1}$

Figs 9–12 are indicative of changes to the bending vibrations of isolated and geminal silanols. Though there is some debate as to assignments in this region, a peak around 600 $\text{cm}^{-1}$ has been assigned to in-plane bending of geminal silanols. The peak at 800 $\text{cm}^{-1}$ is almost certainly associated with fundamental Si-O vibrations, though the shoulder at 740 $\text{cm}^{-1}$ may be due to OH bending of silanols. The intensity of the absorptions in this region is low and as such any changes cannot be readily quantified. However, if these absorption do indeed correspond to isolated and geminal silanols, there is some suggestion from the spectra that the more basic adsorbates, especially those containing the unsaturated carbonyl group, interact with these sites.

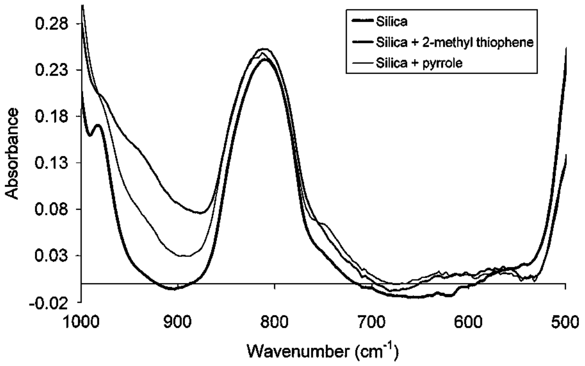


*Figure 9* Infrared spectra of silica in the range 1000–500 $\text{cm}^{-1}$, showing the adsorption of 2-methylthiophene and pyrrole.

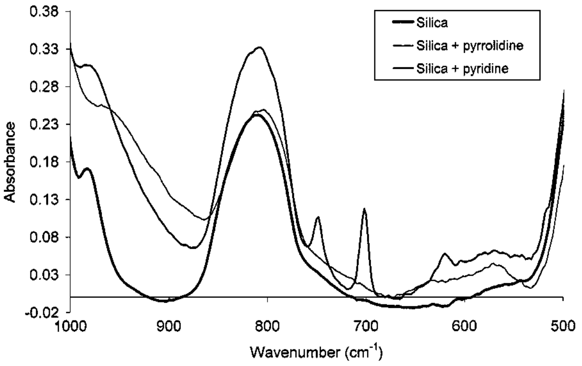


*Figure 10* Infrared spectra of silica in the range 1000–500 $\text{cm}^{-1}$, showing the adsorption of pyrrolidine and pyridine.

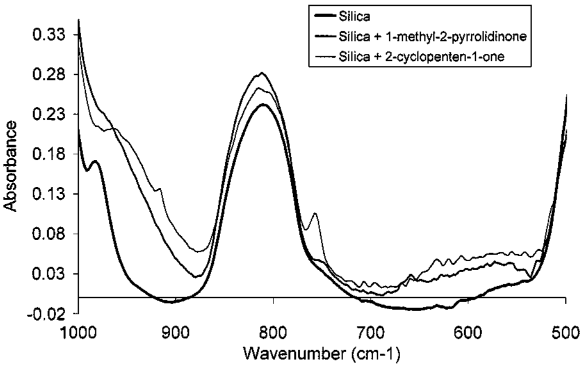


*Figure 11* Infrared spectra of silica in the range 1000–500 $\text{cm}^{-1}$, showing the adsorption of 1-methyl-2-pyrrolidinone and 2-cyclopenten-1-one.

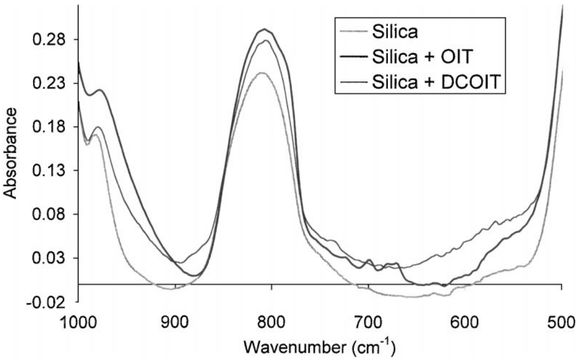


*Figure 12* Infrared spectra of silica in the range 1000–500 $\text{cm}^{-1}$, showing the adsorption of OIT and DCOIT.

## 4. Conclusions

This study has demonstrated that FMC may be used to probe acid-base interactions in silicas. Both the enthalpies of acid-base association and amounts of adsorbates retained by a siliceous framework were determined, and the enthalpies obtained were validated by values from the literature. The FMC cell provided the facility to recover the silica and analyse the modified adsorbent by spectroscopic methods. The value of being able to quantify the strength and nature of associations using the same sample source is self-evident.

For silica that had been thermally pre-treated it was shown that heterocyclics with five-membered rings preferentially adsorbed to isolated and/or geminal silanol groups remaining on the surface. The strength of the interaction was a function of the relative basicity, polarity and $\pi$-character of the heterocyclic. Although increasing basicity enhanced the adsorption enthalpy and hence the strength of associations, desorption was inhibited when a carbonyl, or unsaturated carbonyl, group was adjacent to the active basic centre. Bulky electron-withdrawing agents (chlorine atoms) substituted at the double bond of the unsaturated carbonyl reduced the adsorption considerably. This was attributed partly to steric hinderance restricting the proximity of the basic groups with the active silanol sites. In this context there is some suggestion that the planarity of the organic adsorbate may be an important factor determining the stability of acid-base associations on the silica surface.

Without further study it is difficult to make more definite conclusions regarding the observed adsorption activity of the heterocyclics. Although silanol groups are weakly acidic the relative strength of specific types of silanol will vary. This feature coupled with their distribution and accessibility is clearly a defining factor in adsorption activity. With this in mind the role of the silica will be the subject of Part II of this paper.

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