Pore Constraints in the Novel High-silica Zeolite HFu-1

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Summary Base adsorption properties of the new high-silica zeolite HFu-1, studied by i r spectrophotometry are such that Me_3N and pyridine do not have access to the internal acid sites of this zeolite, the size constraint of about 0 5 nm is in marked contrast to that of ZSM-5 which will admit aromatic compounds

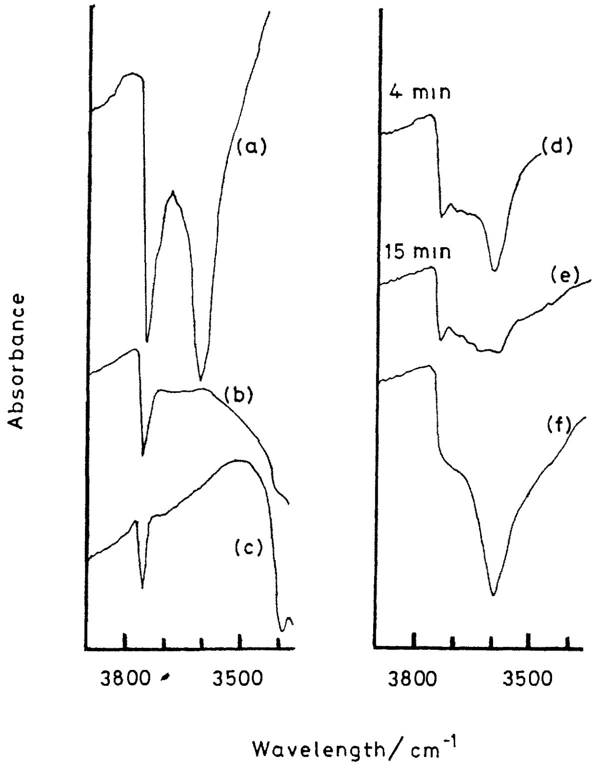

FIGURE Spectra of zeolite HFu 1 (a) After evacuation at 450 °C for 16 h and in the presence of bases (b) NH_3 (40 Torr) (c) $MeNH_2$ (30 Torr) (d) and (e) Me_2NH (5 Torr) showing slow uptake and (f) pyridine (0 5 Torr 16 h at 50 °C)

DURING the past few years high-silica zeolites have aroused considerable interest largely as a result of the reports by Mobil Oil of the conversion of methanol into gasoline over the zeolite ZSM-5 [1] Synthesis of this material involved the use of tetra-n-propylammonium ions but the use of other tetra-alkylammonium ions has led to a number of other novel high-silica zeolites, and Fu-1,[2] prepared in I C I Ltd Laboratories, is one of these A recent report by Vedrine *et al* [3] details the study of ZSM 5 by i r , microcalorimetry, and e s r techniques We describe here some work aimed at the characterisation of zeolite Fu-1 Some catalytic work with HFu-1 has already been reported [4]

This zeolite was prepared according to the patent literature[2] and subsequently exchanged and calcined to yield its acid form with an approximate Si Al ratio of 14 · 1 Wafers about 10—20 mg in weight were prepared from HFu-1 by pressing the powder in a 15 mm diameter die at about 1 75 tonnes Each wafer was mounted for study in a stainless steel disc holder which was positioned in a vacuum cell with windows of single crystal silicon The cell was arranged so that the wafer was in the sample beam of a Perkin Elmer 257 grating i r spectrophotometer After evacuation of the sample for 16 h at 723 K, a pressure of $1{\cdot}4 \times 10^{-3}$ Pa was found and the spectrum of the zeolite recorded in the hydroxyl region The zeolite samples could then be exposed to various adsorbates and treatments and the effect on the i r spectrum was monitored Use of this technique of examining zeolite surfaces and surface reactions has been well reviewed by Ward [5]

Some of the spectra obtained are shown in the Figure That of the 'degassed' zeolite [Figure (a)] consists essentially of two hydroxyl bands at 3740 and 3600—3610 cm^{-1} and the acidity of the hydroxyl groups can be determined by the use of ammonia as an adsorbate Chemisorption of the OH groups responsible for the latter band results in the formation of an ammonium ion identified by a broad absorption at 1450 cm^{-1} The absorption at 3740 cm^{-1} is affected only by physical adsorption and the base is readily removed

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by evacuation at 323 K, showing the relatively weak acidity of these hydroxyl groups. This is in line with the normal assignment of bands at about 3740 cm^{-1} to surface silanol groups.[5] Whereas ammonia and methylamine had ready access to the acidic groups [Figure (b) and (c)], trimethylamine and pyridine were unable to perturb or chemisorb these sites. Indeed, even after 16 h at 323 K pyridine had not gained access [Figure (f)]. Dimethylamine reacted more slowly than the small bases, allowing spectra of partially reacted states to be recorded over about 20 min. Times given in the Figure (d) and (e) relate to the start of each spectrometer scan of the hydroxyl region. It would therefore appear that the acidic sites in HFu-1 are accessible only to molecules with effective diameters less than or equal to that of dimethylamine, *i.e.* smaller than about 0·5 nm. This is confirmed by a study with cyclic ethers where perturbation of an i.r. absorption band indicates accessibility of an ether to that site. The results given in the Table show that oxetan (trimethylene oxide) and oxolan (tetrahydrofuran) cannot physisorb the acidic sites of HFu-1 while oxiran (ethylene oxide) can. The similarity of the size constraint for ethers and amines for HFu-1 indicates that the amine adsorption was not influenced by the formation of immobile protonated species which may have caused pore blocking.

TABLE. Accessibility of acid sites in Fu-1 to cyclic ethers.

Probe molecule	Perturbation of i.r absorption band	
	3740 cm^{-1}	3610 cm^{-1}
Oxiran	+	+
Oxetan	+	−
Oxolan	+	−

Although pyridine did not have access to the acidic hydroxyl groups responsible for the 3610 cm^{-1} absorption band, it was noted that a small amount of pyridine had been chemisorbed by the zeolite. After adsorption of methylamines, evacuation at 423 K for many hours led to no recovery of the band at 3610 cm^{-1} nor to any diminution of the CH stretching bands. This situation was taken to be a suitable criterion for complete chemisorption to be applied to site-counting by microbalance techniques. The results of this study will be reported in due course.[6]

A linear correlation between the silica to alumina ratio and the frequency of the absorption band due to the acid hydroxyl groups in zeolites was noted recently by Barthomeuf.[7] However, the highest silicon to aluminium ratio in her data was that for mordenite (Si/Al = 5) which has its i.r. band at 3610 cm^{-1}. Data are now available from our work and that of Vedrine[3] which show that the high silica zeolites with Si/Al ratios in the range 12–25 also have bands in the region of 3600 cm^{-1}. These observations show that there is a sharp break to a constant i.r. frequency at the Si/Al ratio of mordenite. Below this ratio statistically the acid sites are effectively isolated and variations in frequency may be attributed to hydrogen bonding interactions with the lattice.

It is clear from the experimental evidence that although HFu-1 is a high-silica zeolite it possesses properties which are significantly different from those of the better known ZSM-5 family. Indeed, the studies of Anderson *et al.*[8] and Vedrine *et al.*[3] show the accessibility of the acid sites of ZSM-5 to aromatic molecules whereas such molecules cannot enter the pore system of HFu-1.

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