

Adsorption of Benzene and Ethylbenzene on the Acidic and Basic Sites of Beta Zeolite

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The adsorption of benzene on Na beta and Cs beta followed by IR spectroscopy shows two pairs of CH out-of-plane bands. They are assigned to benzene interacting with either the cations, acidic sites or the oxygen of the 12-R window, basic sites. Ethylbenzene interacts only with the cations. In addition species similar to liquid benzene are detected below saturation of the adsorption sites. The basicity of the oxygen is higher than that predicted from the Al content. This may result from a specific structure influence.

Beta zeolite has been demonstrated to be useful as a catalyst in several hydrocarbon conversion processes [ref. (1) and (2) and references therein] and as sorbent in separation of aromatics [ref. (3) and (4) and references therein]. Its structure has been recently published^{2,5} and shows the existence of channels with 12-R apertures. The understanding of the adsorption mode of hydrocarbons is of interest since it may explain the behaviour and reactivity of the molecules in the pores. The present study is devoted to the adsorption of two aromatics, benzene and ethylbenzene, in order to characterize the specific sites of adsorption.

Experimental

Materials

The starting material is a beta zeolite of which the composition for 64 T atoms per unit cell² is $\text{Na}_{1.1}(\text{TEA})_{4.9}(\text{AlO}_2)_{6.0}(\text{SiO}_2)_{58.0}$. The tetraethylammonium cations (TEA) are decomposed by heating at 823 K in an oven. The zeolite is then exchanged three times at room temperature with 1 mol dm⁻³ sodium chloride or 0.5 mol dm⁻³ caesium chloride solutions then washed and dried. The chemical compositions of the samples Na beta and Cs beta are, respectively, $\text{Na}_{3.9}\text{H}_{1.6}(\text{AlO}_2)_{5.5}(\text{SiO}_2)_{58.5}$ and $\text{Cs}_{3.7}\text{Na}_{0.6}\text{H}_{1.0}(\text{AlO}_2)_{5.3}(\text{SiO}_2)_{58.7}$ for the same T atom number.

IR Measurements

The studies were carried out on self-supporting wafers of Na beta and Cs beta zeolite (15 mg for 18 mm diameter). The wafers were evacuated at 723 K for 15 h, then treated with a 150 Torr‡ oxygen at 723 K for 15 h as in ref. (6). All IR spectra were recorded at room temperature with a Perkin-Elmer 580 B spectrophotometer equipped with a data station. The spectroscopic slit width was less than 1 cm⁻¹. The spectra were usually accumulated ten times in the region of CH out-of-plane vibration (2050–1700 cm⁻¹).

Adsorption of Aromatics

The adsorption of benzene and ethylbenzene was performed at room temperature on the wafers placed in the IR cell by admitting known amounts of aromatics, step by step. 1 h equilibration was allowed at each stage. The spectrum of the

adsorbed phase was obtained in absorbance after subtraction of the zeolite contribution.

Pyrrole Adsorption

Freshly distilled pyrrole was adsorbed at room temperature by contacting the vapour of the liquid for 10 min or 1 h at room temperature before recording the spectra.

Results

Benzene Adsorption

Fig. 1 shows the IR spectra in the 4000–1200 cm⁻¹ region of Na beta [spectrum (a)] and Cs beta [spectrum (d)] after activation of the samples at 723 K. Both spectra show three bands of hydroxyls at 3746, 3673 and 3560 cm⁻¹ and intense zeolite bands in the range 1500–2300 cm⁻¹.

After adsorption of 6.6 molecules of benzene per unit cell (i.e. 6.6 mol/u.c.) [spectrum (b) fig. 1] on Na beta the bands at

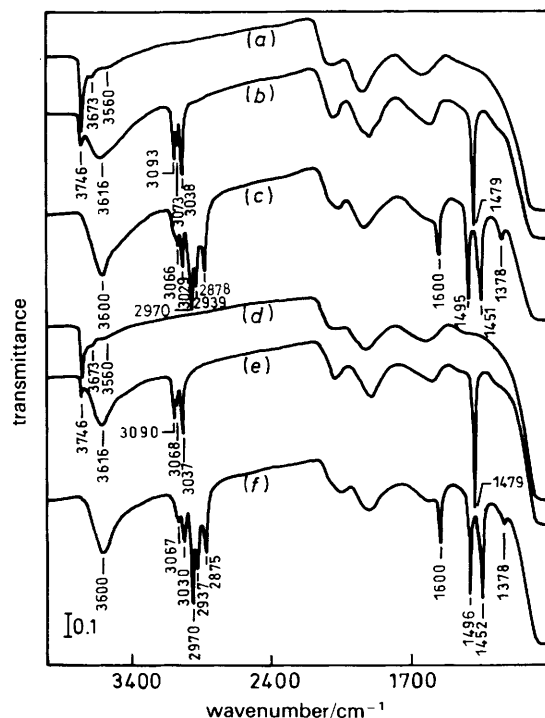


Fig. 1. IR spectra of benzene and ethylbenzene adsorbed on Na beta [(b) and (c)] and Cs beta [(e) and (f)]: (a) pure Na beta; (b) 6.6 molecules benzene/u.c.; (c) 4.1 molecules ethylbenzene/u.c.; (d) pure Cs beta; (e) 6.9 molecules benzene/u.c.; (f) 3.9 molecules ethylbenzene/u.c.

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‡ 1 Torr \approx 101 325/760 Pa.

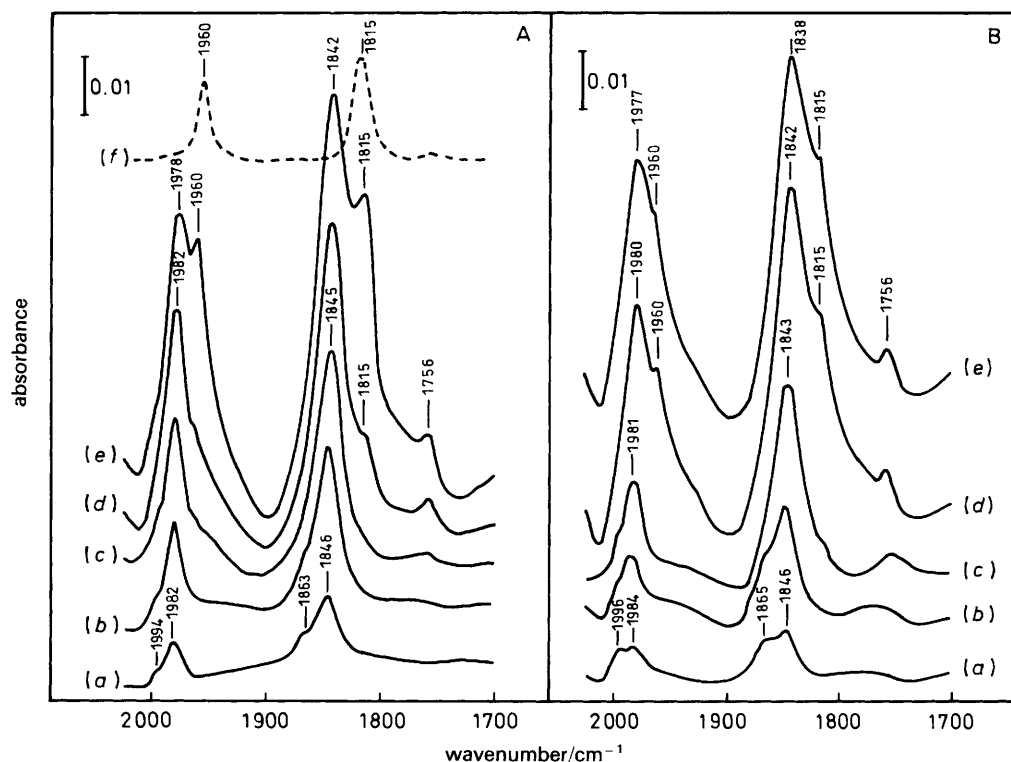


Fig. 2. IR spectra of benzene adsorbed on Na beta (A) and Cs beta (B) at room temperature in the CH out-of-plane range as a function of loading. Loadings in molecules per u.c. on Na beta, (a) 0.5; (b) 1.4; (c) 2.1; (d) 3.8; (e) 6.6 and (f) pure liquid; on Cs beta, (a) 0.54; (b) 1.38; (c) 2.1; (d) 3.9 and (e) 6.9.

3673 and 3560 cm^{-1} disappear and a band at 3616 cm^{-1} is formed. After evacuation at room temperature for 2 min the 3616 cm^{-1} band decreases and the other three increase. Simultaneously with the aromatic adsorption, bands of benzene are observed at 3093, 3073, 3038, 3011 and 1479 cm^{-1} . The spectra are comparable to that of liquid benzene. The shifts usually obtained for benzene in faujasite for CH out-of-plane bands in the range 1800–2100 cm^{-1} cannot be detected in spectra 1(b) because of the broad zeolite bands in this range which hide almost all the benzene bands. Subtraction of the zeolite contribution gives the spectra of fig. 2A for Na beta in the CH out-of-plane range. They are obtained for increasing loadings with at least 10 times spectra accumulation. Similar results are obtained after adsorption of 6.9 molecules per u.c. on Cs beta [fig. 1(e) and 2B]. Compared to the pure liquid [fig. 2A(f)] the CH out-of-plane vibrations of benzene on Na beta or Cs beta are disturbed. The pair of bands at 1815 and 1960 cm^{-1} are shifted to high wavenumbers and each band is split into doublets upon adsorption of low amounts of the hydrocarbon on both zeolites. Adsorption of 0.5 molecules per u.c. on Na beta shows the existence of two doublets forming, in fact, two pairs of CH bands. The one consists of the bands at 1846 and 1982 cm^{-1} and the second pair is formed with 1863 and 1994 cm^{-1} bands. With increased loading the intensities of the bands at 1846 and 1982 cm^{-1} increase very rapidly and their wavenumbers are shifted to lower values, while progressively only shoulders are observed at the wavenumbers 1863 and 1994 cm^{-1} . With further increase in loading, bands similar to those of liquid benzene at 1960 and 1815 cm^{-1} are observed to form a third pair. In the case of benzene adsorption on Cs beta zeolite a similar situation occurs at low loading, the wavenumbers of the first two pairs are observed at 1846–1984 cm^{-1} and 1865–1966 cm^{-1} [fig. 2B(a)]. The main difference with Na beta is the ratio of the absorbance of the two pairs which is closer to a value of one in Cs beta than

in Na beta. As previously, at increased benzene loading only the absorbance of the pair at 1846 and 1984 cm^{-1} increases simultaneously with a shift to lower frequencies [for instance 1838–1977 cm^{-1} in spectrum (e) fig. 2B]. The bands with wavenumbers of liquid benzene appear at similar loading.

The behaviour of adsorbed benzene after evacuation at increasing temperatures for 2 min is reported in fig. 3A and 3B for Na beta and Cs beta, respectively, in the same range as in fig. 2. The reversibility of the shape of the spectra is noticeable with first the disappearance of bands corresponding to liquid benzene. For spectra with similar shapes in fig. 2 and 3 the wavenumbers are the same. The adsorbed benzene disappears completely at 423 K from Cs beta and at 473 K from Na beta.

Ethylbenzene Adsorption

Fig. 1 [spectra (c) and (f)] shows the IR spectra of ethylbenzene after adsorption of 4.1 and 3.9 molecules per u.c. on Na beta and Cs beta, respectively. No bands are observed at 3673 and 3560 cm^{-1} ; the band of terminal OH groups at 3746 cm^{-1} disappears and a new broad and intense band is formed at 3600 cm^{-1} . After evacuation at room temperature for 2 min the intensity of this band decreases, but only the 3746 cm^{-1} band is partly restored. Before evacuation bands are observed in the range of C–H stretching and deformation vibrations at 3105, 3085, 3066, 3029, 2970, 2937, 2902, 2878, 1600, 1495, 1460, 1451 and 1378 cm^{-1} as in liquid ethylbenzene. As in the case of benzene adsorption, the bands in the 2200–1700 cm^{-1} region are hidden in the zeolite bands. Subtraction of those bands give the spectra of fig. 4. Fig. 4A describes the changes observed for ethylbenzene adsorbed in Na beta at room temperature in the CH out-of-plane region for different loadings. The spectra obtained with Cs beta are very similar. In both cases the bands are shifted by ca. 30 cm^{-1} to higher wavenumbers compared to liquid ethylbenzene [spectrum (e)].

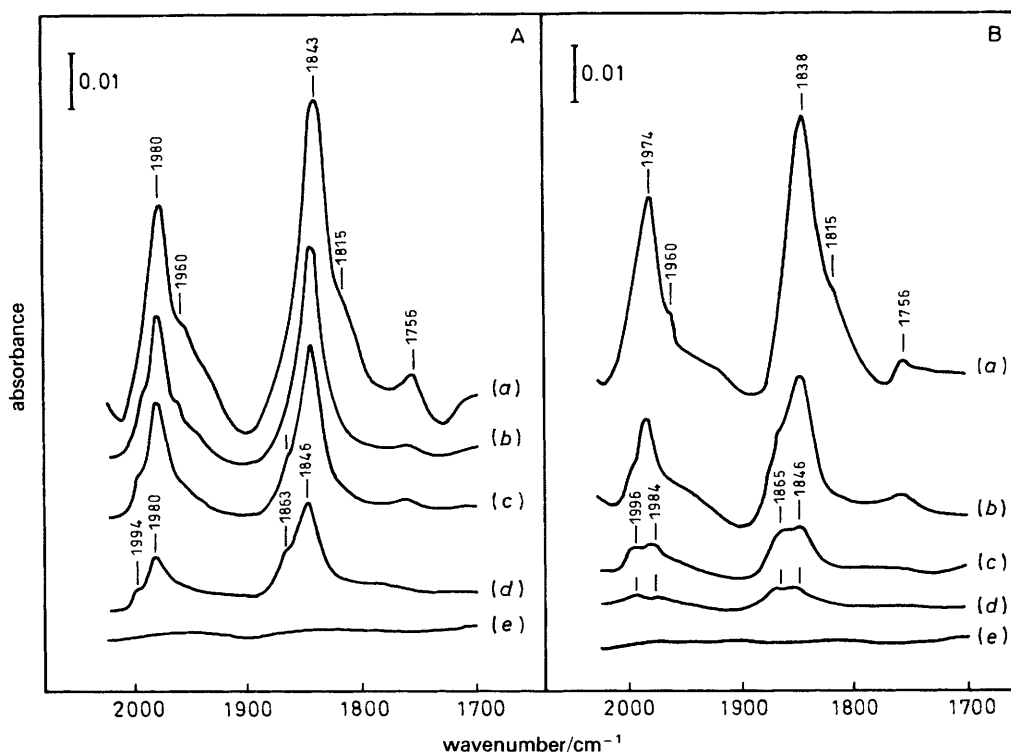


Fig. 3. IR spectra of benzene adsorbed on Na beta (A) and Cs beta (B) after desorption at various temperatures (in °C). On Na beta, (a) room temperature; (b) 70; (c) 100; (d) 150 and (e) 200; on Cs beta, (a) room temperature; (b) 70; (c) 100; (d) 120 and (e) 150.

The spectra are more complex than for benzene since four bands plus three shoulders are present in the liquid. No splitting of the bands is detected for the adsorbed forms. After adsorption of a small amount of ethylbenzene [0.4 molecules

per u.c. spectrum (a)] several bands are observed at 1776, 1833, 1848sh, 1893, 1906, 1963 and 1978 cm⁻¹. At a loading of 1.2 molecules per u.c. the bands of liquid ethylbenzene appear [spectrum (c)] at 1746, 1801, 1862 and 1943 cm⁻¹.

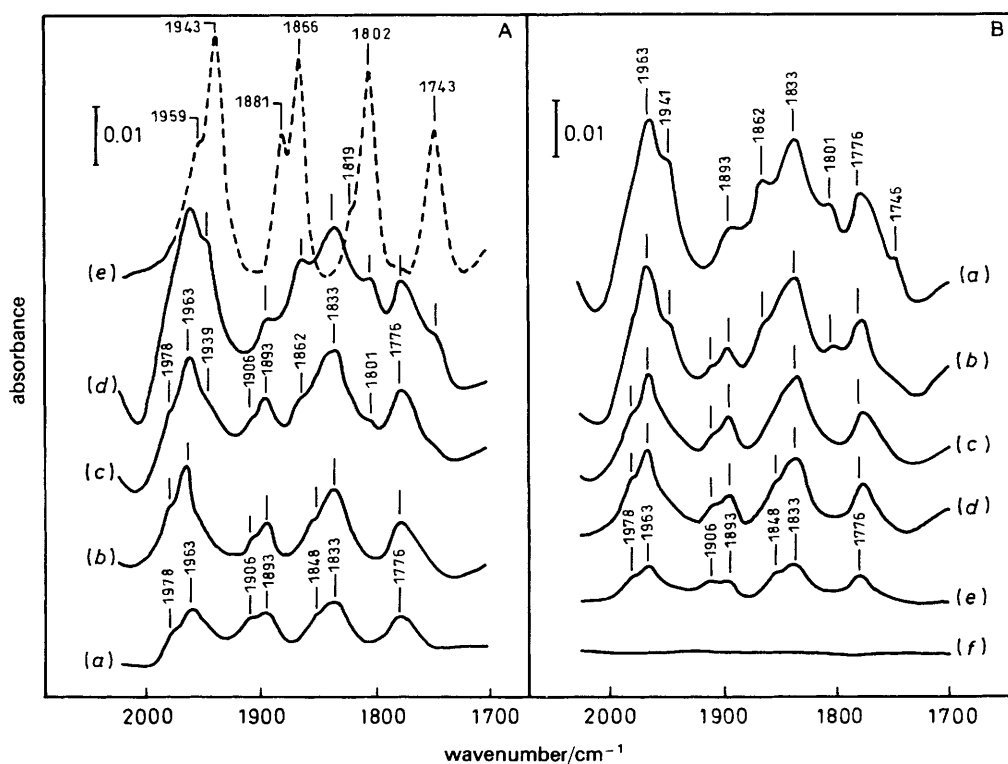


Fig. 4. IR spectra of ethylbenzene adsorbed on Na beta at room temperature (A) and desorbed at different temperatures (B). Adsorption in molecules per u.c. (a) 0.4; (b) 0.86; (c) 1.2; (d) 2.2 and (e) pure liquid. Desorption (in °C) at (a) room temperature, (b) 70; (c) 120; (d) 150; (e) 200 and (f) 250.

The intensities of all these bands increase with the amount of ethylbenzene adsorbed and their wavenumbers do not change with loading.

The desorption of ethylbenzene from Na beta upon evacuation at different temperatures for 2 min is shown in fig. 4B. As with benzene the adsorption-desorption process is reversible, giving spectra with similar shapes. Ethylbenzene is fully desorbed from Na beta after evacuation at 523 K. Similar results are obtained for Cs beta, the zeolite being free of ethylbenzene after evacuation at 453 K.

Pyrrole Adsorption

After adsorption of pyrrole at room temperature on Cs beta and Na beta the bands characteristic for NH stretching vibration⁷ are observed at 3404 and 3394 cm^{-1} , respectively. Simultaneously the bands of OH groups at 3746, 3673 and 3560 cm^{-1} disappear from the spectrum, showing an interaction of OH with pyrrole owing to the amphoteric character of this probe molecule.

Discussion

Band Assignment

In liquid benzene bands have been assigned⁸ to stretching CH and combination of bending C—C in the range 3030–3100 cm^{-1} , to combination bands of CH bending modes (CH out of plane) at 1815 and 1960 cm^{-1} and to ring deformation at 1479 cm^{-1} . The 1815 and 1960 cm^{-1} bands are assigned to the $\nu_{10} + \nu_{17}$ and $\nu_5 + \nu_{17}$ vibrations, respectively. Upon adsorption of benzene on NaY^{9,10} or CaY⁹ a shift to high wavenumbers of this pair of bands occurs and each band is split into two components. A detailed study of a large number of various alkali-metal-cation faujasites with different Al contents and benzene loadings was made.¹¹ The two pairs of bands resulting from the split of the starting pair are referred to as the low-frequency (LF) and high-frequency (HF) pair. All the results support the hypothesis that the low-frequency pair of bands can be assigned to benzene interacting with cations through the Π cloud and the high-frequency pair of bands would result from CH weak interaction with the framework oxygen.^{6,11–13} It was also shown that the extent of each type of interaction depends on the Lewis acidity of the cation and on the oxygen basicity. This means that zeolites with the lowest basicity do not adsorb benzene in the 12-R window. This is observed for LiY and NaY at low benzene loading and HY at any loading. Those systems give only the LF pair of bands. Fig. 2 shows some similarities in the behaviour of benzene adsorbed on Na beta and Cs beta or on faujasite. The LF pair of bands present at low loading can be assigned to interaction with Na cations (bands at 1846–1982 cm^{-1}) or Cs cations (bands at 1846 and 1984 cm^{-1}). In addition, the interaction with OH groups may contribute to these bands. Beta zeolite has 12-R windows^{2,5} as faujasite which can accommodate benzene molecules. It is proposed that the HF pair of bands results from interaction between framework oxygen and benzene (bands at 1863–1994 cm^{-1} in Na beta and at 1865–1996 cm^{-1} in Cs beta). The presence of those bands at low loading suggests that basicity of the two beta zeolites studied is high enough. Starting at loadings of 3.8–3.9 molecules per unit cell bands appearing at similar wavenumbers as in liquid benzene are observed at 1815–1960 cm^{-1} for the two zeolites.

The ethylbenzene assignments are made by comparison to toluene assignments.¹⁴ The bands of fig. 4 correspond to the overtones and combinations. The absence of any splitting suggests that ethylbenzene is adsorbed on a single type of site at any loading on both zeolites. In contrast to benzene, ethyl-

benzene is too bulky to sit flat in the 12-R window of beta zeolite. Ethylbenzene is also more basic than benzene¹⁵ which would restrict its tendency to interact with basic sites. In addition, the shifts from liquid observed upon ethylbenzene adsorption on Na or Cs beta are *ca.* 20–30 cm^{-1} , which is comparable to those obtained upon benzene adsorption on Na or Cs cations in beta (fig. 2). They are lower than the 35–50 cm^{-1} shifts observed for the HF pair, *i.e.* for benzene interacting with oxygen. Those observations suggest that ethylbenzene would interact with hydroxyls and Na or Cs cations in beta zeolite and not significantly with framework oxygen. The shifts observed in fig. 4 would depict this interaction. Bands at wavenumbers similar to those of liquid ethylbenzene are observed at loadings in molecules per unit cell between 1.2–1.8 for Na beta and 0.9–1.2 for Cs beta.

Quantitative Approach and Strength of Adsorption

The total capacity of adsorption of benzene in beta zeolite can be estimated from literature results.¹⁶ Assuming the same number of adsorbed molecules for benzene or cyclohexane one can evaluate that Na beta and Cs beta will adsorb at saturation *ca.* 9.6 benzene molecules per unit cell.¹⁷ For ethylbenzene this capacity is estimated from ref. (3) to be *ca.* 8.7 molecules per u.c. for Na beta and 7.5 molecules per u.c. for Cs beta.

An estimation of the number of potential cationic adsorption sites can be made from the above unit cell formulae. It follows that 70% of cationic sites exchange Na^+ ions or Cs^+ cations. This is in agreement with ref. (16). The 30% left are inaccessible in cages having apertures probably not larger than 6 rings, *i.e.* cages not accessible to aromatics. One could expect that at least the exchangeable alkali-metal cations, *i.e.* *ca.* 3.7 ions per unit cell, and possibly a part of the protons, due to their mobility, should be accessible to aromatics. The total number of adsorption sites should be higher for benzene since in addition it should include some 12-R windows.

Fig. 2 and 4 show that bands similar to those of the liquid appear at loadings between 2.1–3.8 molecules per u.c. for benzene in both zeolites and 1.2–1.8 for ethylbenzene on Na beta. The value goes down to 0.9–1.2 for this aromatic on Cs beta. Those values are lower than the saturation of the potential adsorption sites. It appears that some form of adsorbed aromatics giving infrared bands at the same wavenumbers as liquids are present before all the specific adsorption sites are filled. Several hypotheses may be considered to explain those results. In Y or X faujasites such bands are not observed even at high loadings.^{6,13} One may suggest that the diffusion of the aromatics is rather lower than in faujasites. Only an external shell of each beta zeolite crystallite would adsorb benzene or ethylbenzene in the present experimental conditions first on specific sites and after their saturation, as a condensed phase. The thickness of this shell would parallel the increase in loading giving a simultaneous rise in the absorbance of all the infrared bands. According to this hypothesis upon desorption the inner parts of the crystal would retain at low loading the aromatics both adsorbed on specific adsorption sites and as a liquid-like form, while the outer shell would be fully desorbed. This is not observed in fact upon evacuation (fig. 3 and 4B) since the spectra are quite reversible, showing no bands at liquid wavenumbers at low loadings. It follows that the distribution of the aromatics in the bulk of the crystals has to be homogeneous. In that case an alternative explanation to the results would be that due to the array of highly intersecting channels in three directions,^{2,5} the chances of having very close adsorbed aromatics at some places would be higher than in faujasites. They could, beyond a given loading, form clusters giving the liquid-like infrared

bands in parallel with a growing amount of aromatic specifically adsorbed on sites.

As to the strength of adsorption, results show that lower temperatures are required in our experimental conditions for complete desorption of the two aromatics from Cs beta than from Na beta. This may arise from a stronger interaction of the aromatics with the more acidic Na^+ ions.

Specific Properties of Beta Zeolite

It is well accepted that highly siliceous zeolites have strongly acidic sites. The existence of conjugate acid–base pairs in zeolites suggests that they would be associated with weak basicity.^{18,19} The Sanderson intermediate electronegativity S^{20} gives an approach to the strengths of protonic acidity²¹ and of basicity^{18,19,21} of zeolites. The values calculated as in ref. (20) depend only on the Al content. For the usual forms of Y (Si/Al = 2.5), ZSM-5 (Si/Al = 24) or the present beta (Si/Al = 9.6) the values for the protonic materials decrease from HY to H beta and then HZSM-5 (table 1) which is the order of the Al content. The charge on proton increases and that on oxygen decreases in the same sequence. For the alkaline cations counterpart the changes are in the same direction. These results are in line with the trends usually observed for the relationship between the Al content and the acid–base properties of zeolites. As to the beta zeolite, results of acid catalysis in the conversion of $n\text{-C}_{13}$ alkanes gives isomerization selectivity characteristic of a zeolite with no very strongly acidic sites.¹ The present results on pyrrole adsorption give NH wavenumbers close to 3400 cm^{-1} for Na beta and Cs beta. The shift $\Delta\nu(\text{NH})$ from the reference value of 3430 cm^{-1} expresses the basic strength. It indicates the presence of basic sites (table 1). A comparison with other zeolites^{18,19} given in table 1 suggests a basic strength in the beta samples comparable to that of NaY and rather higher than that of ZSM-5, i.e. higher than what is expected. It follows that acid–base properties of beta zeolite are not in agreement with the general correlation observed between the acid–base strength and the Al content. The acidity is weaker and the basicity stronger than one would predict. This may explain why benzene is able to interact with oxygen of the 12-R windows in Na and Cs beta as seen in fig. 2 and 3. Their basicity, equal at least to that of NaY, is strong enough to initiate an interaction between oxygen and CH groups. Fig. 2 [spectra (a) and (b)] and 3 [spectra (c) and (d)] also show a higher absorbance for the HF pair in Cs beta than in Na beta which is in line with the usually higher basicity of the Cs zeolites.

Mordenite was a previous example of a zeolite having basic sites stronger than calculated. This was explained as due to an influence of the higher intrinsic ionicity evidenced for the mordenite structure^{22,23} which is not taken into account in the S values calculated as in ref. (20). One may suggest that the structure of beta is even more efficient than that of mordenite in influencing the inhomogeneity of charge distribution on the atoms. This would increase the charge on some oxygens, making them more strongly basic than the mean calculated value suggests.

Conclusion

Beta zeolite adsorbs benzene and ethylbenzene in a manner comparable to that of faujasite. Some special features are evi-

Table 1. Intermediate electronegativity, S , partial charge on proton, q_{H} , and on oxygen, q_{O} , and shift in NH pyrrole vibration, $\Delta\nu_{\text{NH}}$

materials	Si/Al	S	q_{H}	q_{O}	$\Delta\nu(\text{NH})$
HY	2.5	4.095	0.139	−0.234	
NaY	2.5	3.538		−0.352	ca. 30
H beta	9.6	4.222	0.171	−0.208	
Na beta	9.6	4.069		−0.240	ca. 30
H ZSM-5	24	4.231	0.173	−0.206	
Na ZSM-5	24	4.140		−0.225	0

denced such as the presence of benzene behaving as a liquid below saturation of the adsorption sites or the interaction with oxygen revealing the existence of unexpected basicity. In that sense the beta structure appears of particular interest in generating specific properties.

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References

1 J. A. Martens, J. Perez-Pariente and P. A. Jacobs, *Proc. Int. Symp. Zeolite Catal.*, Siofok, *Acta Phys. Chem. Szeg.*, 1985, 487.
2 M. M. J. Treacy and J. M. Newsam, *Nature (London)*, 1988, 332, 249; J. M. Newsam, M. M. J. Treacy, W. T. Koetsier and C. B. De Gruyter, *Proc. R. Soc. London, Ser. A*, 1988, 420, 375.
3 D. Barthomeuf and D. D. Rosenfeld, U.S. Patent 4.554.398, 1985; D. Barthomeuf, unpublished results.
4 D. Barthomeuf, U.S. Patent 4.584.424, 1986.
5 J. B. Higgins, R. B. La Pierre, J. L. Schlenker, A. C. Rohrman, J. D. Wood, G. T. Kerr and W. J. Rohrbaugh, *Zeolites*, 1988, 8, 446.
6 A. de Mallmann and D. Barthomeuf, *Proc. 7th Int. Zeolite Conf.* (Kodansha–Elsevier, Tokyo, 1986), p. 609.
7 P. O. Scokart and P. G. Rouxhet, *J. Chem. Soc., Faraday Trans. 1*, 1980, 76, 1476.
8 R. D. Mair and D. F. Horning, *J. Chem. Phys.*, 1949, 17, 1236.
9 M. Primet, E. Garbowski, M. V. Mathieu and B. Imelik, *J. Chem. Soc., Faraday Trans. 1*, 1980, 76, 1942.
10 B. Coughlan, W. M., Carroll, P. O'Malley and J. Nunan, *J. Chem. Soc., Faraday Trans. 1*, 1981, 77, 303.
11 A. de Mallmann, *Thesis* (Paris, 1986).
12 A. de Mallmann and D. Barthomeuf, *J. Chem. Soc., Chem. Commun.*, 1986, 90, 1311.
13 A. de Mallmann and D. Barthomeuf, *Zeolites*, 1988, 8, 292.
14 C. Lalau and R. G. Snyder, *Spectrochim. Acta, Part A*, 1971, 27, 2073.
15 H. H. Perkampus, in *Adv. Phys. Org. Chem.*, 1966, 4, 195.
16 H. E. Robson and A. E. Schweizer, 1984, unpublished, see ref. (2).
17 R. Benslama, J. Fraissard, A. Albizane, F. Fajula and F. Figueras, *Zeolites*, 1988, 8, 196.
18 D. Barthomeuf, *J. Phys. Chem.*, 1984, 88, 42.
19 D. Barthomeuf and A. de Mallmann, in *Innovation in Zeolite Materials Science*, ed. P. J. Grobet et al., *Stud. Surf. Sci. Catal.*, 1988, 37, 365.
20 R. T. Sanderson, in *Chemical Bonds and Bond Energy* (Academic Press, New York, 1976), p. 75.
21 W. J. Mortier, *J. Catal.*, 1978, 55, 138.
22 K. A. Van Genechten and W. J. Mortier, *Zeolites*, 1988, 8, 273.
23 W. J. Mortier, in *Innovation in Materials Science*, ed. P. J. Grobet et al., *Stud. Surf. Sci. Catal.*, 1988, 37, 253.