

QENS and FTIR studies on binding states of benzene molecules adsorbed in zeolite HZSM-5 at room temperature

A. K. Tripathi,^a A. Sahasrabudhe,^a S. Mitra,^b R. Mukhopadhyay,^b N. M. Gupta^{*a} and V. B. Kartha^c

^a Applied Chemistry Division, Bhabha Atomic Research Center, Trombay, Mumbai 400 085, India. E-mail: nmgupta@magnum.barc.ernet.in; Fax: +91 22-5505151

^b Solid State Physics Divisions, Bhabha Atomic Research Center, Trombay, Mumbai 400 085, India

^c Center for Laser Spectroscopy, Manipal Academy of Higher Education, Manipal 576 119, India

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Fourier-transform infrared (FTIR) spectroscopy and quasi-elastic neutron scattering (QENS) were employed for monitoring of the binding states of benzene molecules, adsorbed in HZSM-5 zeolite at 300 K and for loadings of 0.6 to 7 molecules per unit cell. While the in-plane combination C–C and C–H stretching bands of adsorbed benzene remained unaffected, a splitting was observed in the out-of-plane C–H bending vibrational bands, a feature reported for the transformation of benzene from liquid to solid phase. Also, the intensity ratio of the in-plane C–C stretching band (ν_{19}) of adsorbed benzene at 1479 cm^{-1} and the bands in the region $3100\text{--}3035\text{ cm}^{-1}$ due to fundamentals and combination C–C and C–H stretching vibrations indicated a trend observed typically for a condensed phase of benzene. No shift was observed in the frequency of the above-mentioned IR bands when zeolite samples exchanged with Na^+ or Ca^{2+} were employed. QENS results suggest that the benzene molecules occluded in zeolitic pores (~ 3 molecules per unit cell) undergo a 6-fold rotation but their translation motion is too slow. Also, a high residence time of 16.5 ps was observed for the benzene entrapped in HZSM-5, compared to a time of ~ 2.5 ps reported for the liquid and ~ 19 ps for the solid state of benzene. These results reveal again the compression of the benzene molecules on adsorption in zeolitic pores. It is suggested that the benzene molecules confined in cavities experience a strong intermolecular interaction, giving rise eventually to their clustered state depending on the loading. In the clustered state, benzene molecules are packed with their plane parallel to zeolitic walls and interact with each other through π -electron clouds. No electronic bonding is envisaged between these clusters and the framework or the extra-framework zeolitic sites.

Introduction

The influence of pore geometry and of framework acid sites in the catalytic activity and selectivity of zeolites has been under extensive investigation.^{1–4} We have recently demonstrated that, contrary to the earlier studies on adsorption at low temperatures where binding at specific adsorbent sites has been demonstrated,² small molecules such as CO and CO₂ may occlude in the form of molecular clusters [*e.g.*, (CO)_n and (CO₂)_n *etc.*] in the cages of X, Y and ZSM-5 zeolites when adsorbed in a wide pressure range of 10 to 500 Torr and at temperatures in the region 300–400 K.^{5–7} Even though no direct bonding of these molecules at individual zeolitic sites is envisaged, the electrostatic field associated with the charge balancing cations is found to play a crucial role in the binding together of these cluster molecules.^{8,9} The present work extends these previous studies to adsorption of small hydrocarbon molecules in zeolites of ZSM-5 type, the framework of which consists of straight channels interconnected by sinusoidal channels, and there being four channel intersections per unit cell. With a view to examine the dynamics and binding states of benzene molecules adsorbed in the pores of zeolites, we have now undertaken quasi-elastic neutron scattering (QENS) and Fourier-transform infrared (FTIR) spectroscopy measurements to monitor the adsorption of benzene in HZSM-5 under ambient temperature conditions. Comparative

studies were also carried out using NaZSM-5 and CaZSM-5 zeolite samples, in order to explore the possible role of charge balancing cations in the binding of benzene molecules through their π -electrons.

Experimental

Materials

HZSM-5 zeolite ($\text{SiO}_2/\text{Al}_2\text{O}_3 = 30$, surface area $380\text{ m}^2\text{ g}^{-1}$ and pore volume $0.22\text{ cm}^3\text{ g}^{-1}$) was obtained from Zeolite International, USA. A template free NaZSM5 sample ($\text{Si}/\text{Al} = 40$, surface area $454\text{ m}^2\text{ g}^{-1}$, pore volume $0.26\text{ cm}^3\text{ g}^{-1}$) was received from the Research and Consultancy Directorate of the Associated Cement Co. Ltd, Thane, India. A calcium-exchanged sample was prepared by replacing about 57% of Na^+ in NaZSM-5 using a conventional ion-exchange method; the sample was found to have a pore volume of $\sim 0.29\text{ m}^3\text{ g}^{-1}$ after final calcination. The crystallographic integrity of the samples was ascertained using X ray powder diffraction.

Quasi-elastic neutron scattering

About 1.8 g of a zeolite sample was calcined at 773 K before placing in a thin-walled (2 mm) aluminum cell of rectangular shape [100 mm (*h*), 12 mm (*w*)]. The sample thickness was 4 mm. Before adsorption of benzene ($\sim 0.52\text{ mmol g}^{-1}$) at 300

K, the zeolite was heated *in situ* for 48 h at 625 K under a vacuum of 10^{-6} Torr. Neutron transmission measurement on the sample indicated complete adsorption and the amount of benzene thus evaluated matched with the loading value of 3 molecules per unit cell.

The QENS experiments were performed using the medium resolution quasi-elastic spectrometer at Dhruva Reactor at Trombay.¹⁰ The spectrometer is installed at the end of a tube going through the reactor core. It has a double monochromator for variation of the incident energy and an air cushion based spectrometer for energy analysis. A double monochromator placed inside the pile block of the reactor provides a closer approach to the source. Vertically bent crystals¹¹ are used to focus the neutrons at the sample position and thereby enhance the neutron intensity substantially. The spectrometer is used in multi-angle reflecting crystal (MARX) mode¹² where one essentially uses a combination of large analyzer crystal and a linear position sensitive detector, providing larger throughput. This is essential for such experiments to be carried out in a medium flux reactor. PG crystals are used for both double monochromators and analyzer. The resolution of the instrument was obtained by measuring the spectra of ZrH_2 at all the wave-vector transfer (Q) values. In the present configuration the spectrometer has an energy resolution of 200 μ eV with an incident wavelength of 4 \AA . The quasi-elastic spectra of benzene adsorbed in HZSM-5 zeolite were recorded in the Q range of 0.8 to 1.8 \AA^{-1} at 300 K. With the available energy resolution of the spectrometer, diffusion coefficients of the order of 10^{-5} to 10^{-6} $\text{cm}^2 \text{s}^{-1}$ only could be measured.

Infrared spectroscopy

IR spectra were recorded in a stainless steel cell with provision for *in situ* heat treatment to a sample, either under vacuum (1×10^{-4} Torr) or in a gas flow.⁵⁻⁷ A Mattson model Cygnus-100 FTIR spectrophotometer equipped with a DTGS detector was used in transmission mode and 300 scans were collected for each spectrum at a resolution of 4 cm^{-1} . Sample wafers of 2.5 cm diameter were prepared by compressing about 70 mg of powder at 154 MPa pressure. The spectrum of a wafer, recorded after *in situ* pretreatment for 24 h at 625 K under vacuum and prior to adsorption of benzene, was normally taken as background to compensate for the framework IR signals.

Benzene vapor was introduced into the cell at room temperature in the form of benzene (5.5 mol.%) + argon gas mixture, and at doses of 10 to 1000 μmol per gram of sample (corresponding to 0.1 to 7 molecules per unit cell). The resulting pressure in the cell was in the range 1 to 80 Torr; about 1.2 Torr for the lowest benzene dose of 12 $\mu\text{mol g}^{-1}$ and about 80 Torr for a dose of 980 $\mu\text{mol g}^{-1}$. No IR bands due to free benzene vapor were noticed, indicating that most of the benzene was adsorbed into the sample and the pressure in the cell was due exclusively to argon. The absorbance values of individual IR bands were taken as a measure of relative intensity, and are included in parentheses in some of the figures for a comparative evaluation. The overlapping bands in some of the spectra were resolved into Gaussian components of equal width ($\sim 19 \text{ cm}^{-1}$), and the areas under these bands were taken as an estimate of relative intensity. Frequency reproducibility of individual IR bands was of the order of 1 to 2 wavenumbers during repeated experiments. Benzene was distilled twice prior to its use and was free of any impurity, such as moisture.

Results

Quasi-elastic neutron scattering

In general, the dynamics of any molecular system involve two kinds of motions, namely, translational and rotational. Earlier studies^{13,14} have reported a value of 10^{-9} – 10^{-10} $\text{cm}^2 \text{s}^{-1}$ for

the intracrystalline translational diffusion coefficient of benzene in ZSM-5. Since diffusional coefficients of this order are not amenable to detection with our experimental set-up, it has been assumed for the analysis of the present data that the translational motion will not contribute to the quasi-elastic broadening and what is observed is only due to the localized motions, *i.e.* rotations or motions occurring within a restricted volume.

For rotational motion, the incoherent scattering law in general can be written as¹⁵

$$S_{\text{inc}}(Q, \omega) \propto A(Q)\delta(\omega) + [1 - A(Q)]L(\Gamma, \omega) \quad (1)$$

where the first term is the elastic part and the second term is the quasi-elastic part. $L(\Gamma, \omega)$ is a Lorentzian and Γ is the half-width at half-maximum (HWHM) of the Lorentzian function which is inversely proportional to the residence time defined as the time between two successive jumps and the jump is instantaneous. It is convenient to analyze the data in terms of the elastic incoherent structure factor (EISF) which provides information about the geometry of the molecular motions. If $I_{\text{el}}(Q)$ and $I_{\text{qe}}(Q)$ are the elastic and quasi-elastic intensities respectively, the EISF is defined as,¹⁵

$$\text{EISF} = \frac{I_{\text{el}}(Q)}{I_{\text{el}}(Q) + I_{\text{qe}}(Q)} \quad (2)$$

Therefore, $A(Q)$ in eqn. (1) is nothing but the EISF.

In analyzing the data, an unbiased procedure was followed, where no specific model was assumed. The scattering law given by eqn. (1) was convoluted with the instrumental resolution function and elastic and quasi-elastic components in the total spectra were estimated at all Q values by least squares fit.

Fig. 1 shows the QENS spectrum of benzene adsorbed in HZSM-5 zeolite (~ 3 molecules per unit cell) at room temperature. In this figure the elastic (curve a) and quasi-elastic (curve b) parts were separated from the total spectrum (curve c) typically at Q value of 1.32 \AA^{-1} . The elastic incoherent structure factor (EISF), which defines the geometry of molecular motion, was calculated using eqn. (2). These values are given in Fig. 2. Also plotted in Fig. 2 are the theoretical EISF values, calculated by using (i) a jump model among N equivalent sites on a circle¹⁶⁻¹⁸ (curves a and b represent the EISF for 2-fold and 6-fold rotational jumps, respectively) and (ii) an isotropic rotational diffusion¹⁹ (curve c). It is thus apparent that the experimental EISF values, shown by solid circles in Fig. 2, closely follow the 6-fold jump model (curve b). It can thus be inferred that the benzene molecules perform a 6-fold jump rotation in the channels of HZSM-5 zeolite.

To estimate the residence time τ of benzene molecules, the spectra were fitted using the scattering law for 6-fold jump

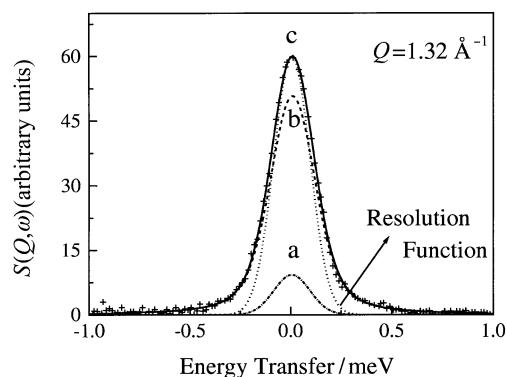


Fig. 1 Separated elastic (curve a) and quasi-elastic (curve b) parts are shown from the total spectrum (curve c) at $Q = 1.32 \text{ \AA}^{-1}$. Dotted line represents the resolution function.

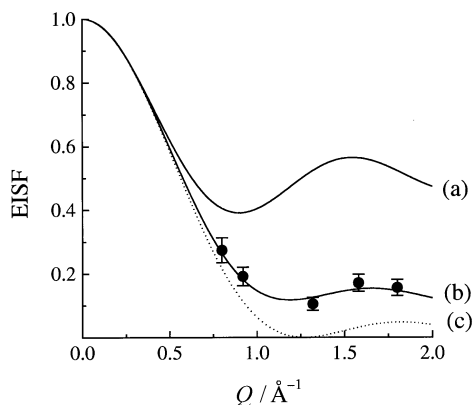


Fig. 2 Elastic incoherent structure factor as a function of wave-vector transfer Q . Curves a and b are theoretical EISF for 2-fold and 6-fold jump models as discussed in the text. Curve c is the theoretical EISF for isotropic rotational diffusion. Symbols represent experimentally obtained EISF.

rotation^{16,17} that is defined as

$$S(Q, \omega) = A_0(Q)\delta(\omega) + \sum_{l=1}^{l=5} A_l(Q) \frac{1}{\pi} \frac{\tau_l}{1 + \omega^2\tau_l^2} \quad (3)$$

with

$$A_l(Q) = \frac{1}{6} \sum_{n=1}^{n=6} j_0(Qa_n) \cos\left(\frac{2ln\pi}{6}\right) \quad (4)$$

where a_n are the jump distances under the effect of $(2n\pi/6)$ rotations and can be written as $a_n = 2a \sin(n\pi/6)$. The τ_l are related to the residence time τ as $\tau_l^{-1} = 2\tau^{-1} \sin^2(\pi l/6)$.

Typical fits thus obtained for Q values of 1.8, 1.32 and 0.8 \AA^{-1} are shown in curves a, b and c, respectively, in Fig. 3. Similarly, perfect fits were observed for the other Q values as well. The fits were very good for all the Q values. The residence time, as obtained from the line widths of the quasi-

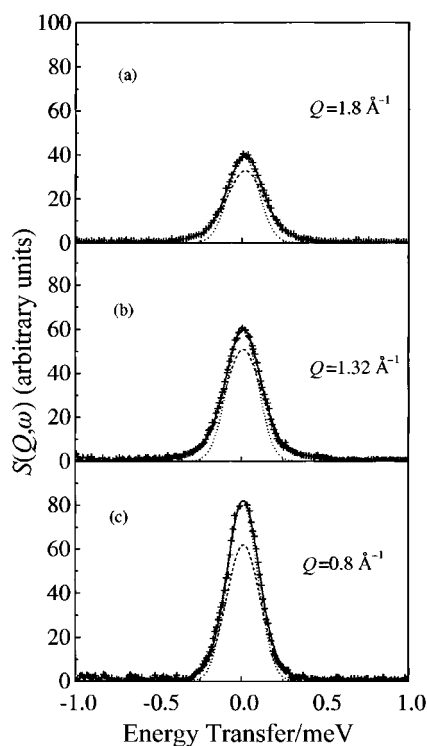


Fig. 3 Fitted spectra at some typical Q values. Dotted line is the resolution of the instrument and dashed line is the quasi-elastic component.

elastic component, was found to be 16.5 ps, which was found to be fairly reproducible during repeated experiments.

Fourier-transform infrared spectroscopy

3000–3100 cm^{-1} region bands. Fig. 4(A) shows the growth of IR bands due to fundamental C–H stretching vibration (ν_{20}) and combination C–C stretching vibrations of benzene with band maxima at 3091 and at 3069 and 3037 cm^{-1} , respectively (spectrum a). While the intensity of these bands increased progressively with the amount of benzene adsorbed, the frequency values were blue shifted only marginally ($\sim 2 \text{ cm}^{-1}$). Table 1 presents the frequency values of the different IR bands observed during the adsorption of benzene over HZSM-5 in this study. Various IR bands reported for liquid and gaseous benzene are also included in this table for comparison. No change was observed in the frequency of these bands on exchanging the protons in HZSM-5 with Na^+ or Ca^{2+} .

1700–2100 cm^{-1} region bands. Spectra a and b in Fig. 5 respectively show out-of-plane C–H vibrational bands of liquid benzene and of benzene adsorbed at a loading of $\sim 490 \mu\text{mol g}^{-1}$ (~ 3.2 molecules per unit cell) in HZSM-5 sample. Spectrum b reveals the presence of multiple overlapping bands, and instead of the 1960 cm^{-1} band for liquid benzene (spectrum a), we see the presence of at least four IR bands at 2006, 1986, 1970 and 1956 cm^{-1} in the case of benzene adsorbed in HZSM-5. Similarly, four bands at 1870, 1850, 1831 and 1811 cm^{-1} appear in place of the 1815 cm^{-1} band of liquid benzene. The relative intensity of these bands depended considerably on the amount of benzene adsorbed and also on the nature of the charge balancing cation. Spectra c and d in Fig. 5 show corresponding data for adsorption of 3.2 molecules of benzene per unit cell in NaZSM-5 and CaZSM-5 zeolites, respectively. From comparison of spectra b–d it is apparent that: (i) the bands mentioned above are more intense and better resolved in the samples containing Na^+ or Ca^{2+} for charge compensation, (ii) the intensity of individual vibrational bands in different samples followed a trend $\text{Ca}^{2+} > \text{Na}^+ > \text{H}^+$ and (iii) no shift is noticed in the frequency of these bands on ion exchange.

The relative intensity of out-of-plane C–H vibrational bands mentioned above depended considerably on the amount of benzene adsorbed, as shown in the spectra given in Fig. 6 for loadings in the range 0.7 to 6 benzene molecules per unit cell of HZSM-5. It is of importance to note that, even for

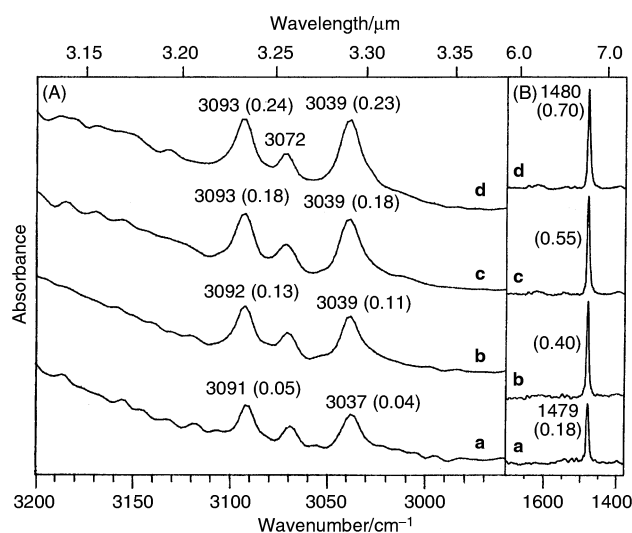


Fig. 4 (A) C–H stretching (ν_{20}) and combination C–C ($\nu_1 + \nu_6 + \nu_{19}$ and $\nu_{19} + \nu_8$) vibrations and (B) in-plane C–C stretching vibration (ν_{19}) of benzene, when adsorbed at different loadings over HZSM-5 zeolite at room temperature: (a) 98.6, (b) 246.4, (c) 492.8 and (d) 985.6 $\mu\text{mol g}^{-1}$.

Table 1 The frequency of the main infrared absorption bands (cm^{-1}) for benzene in the liquid and gaseous phases and on adsorption over HZSM-5 zeolite^{23,28}

C_6H_6 adsorbed on HZSM-5 ($\pm 1 \text{ cm}^{-1}$)	Liquid C_6H_6	Gaseous C_6H_6	Assignment and vibrational mode
3092	3090	3099	C–H stretching (ν_{20})
3070	3070	3073	C–C stretching (ν_1) + C–C–C \parallel bending (ν_6) + C–C stretching (ν_{19})
3039	3035	3045	C–C stretching (ν_{19}) + C–C stretching (ν_8)
1971 1956	1960	1964	C–H \perp bending (ν_5) + C–H \perp bending (ν_{17})
1833 1812	1815	1807	C–H \perp bending (ν_{10}) + C–H \perp bending (ν_{17})
1479	1478	1485	C–C stretching (ν_{19})

a low loading of 0.7 molecules/u.c., the spectrum of adsorbed benzene (spectrum a) is different from that of liquid benzene (cf. Fig. 5 spectrum a). Thus, instead of liquid benzene bands at 1960 and 1815 cm^{-1} , we observe two prominent bands at 1971 and 1832 cm^{-1} showing a shift of 11 and 17 cm^{-1} , respectively. For higher loadings we observe additional bands

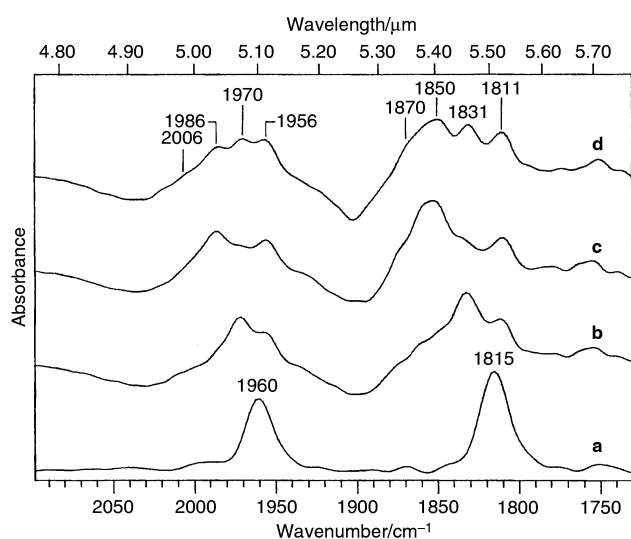


Fig. 5 Comparative C–H out-of-plane vibrations of (a) liquid benzene, and for benzene adsorbed ($\sim 490 \mu\text{mol g}^{-1}$) at room temperature in (b) HZSM-5, (c) NaZSM-5 and (d) CaZSM-5 zeolites.

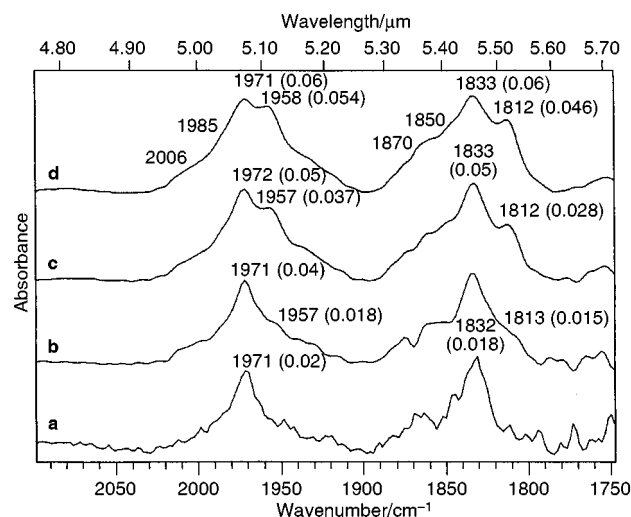


Fig. 6 C–H out-of-plane infrared bands of benzene, adsorbed in different amounts on HZSM-5 zeolite at room temperature: (a) 98.6, (b) 246.4, (c) 492.8 and (d) 985.6 $\mu\text{mol g}^{-1}$.

at 2006, 1987 and 1957 cm^{-1} bands along with the 1971 cm^{-1} band, and similarly additional bands at around 1870, 1850 and 1812 cm^{-1} along with the 1832 cm^{-1} band. The relative intensity of these bands depended upon the amount of benzene adsorbed, as is apparent from the absorbance values given in Fig. 6. Thus, while the intensity of the bands other than the weak bands at 1971 and 1832 cm^{-1} is negligibly small for a loading of 0.7 molecules/u.c., their intensity increased progressively with the amount of benzene adsorbed. Also, the intensity of the pair of bands at 1957 and 1971 cm^{-1} showed a greater increase with increasing amount of benzene adsorbed, compared to the other pair in this region, *i.e.* at 2006 and 1985 cm^{-1} . A similar trend is also seen in the two pairs of bands in the 1900–1750 cm^{-1} region (Fig. 6). Typical values of the relative intensity of the 1957 and 1985 cm^{-1} bands (I_{1957}/I_{1985}) and that of I_{1812}/I_{1850} (as evaluated from the area under these bands) are plotted in Fig. 7 as a function of benzene loading.

1479 cm^{-1} band. A sharp band at 1479 cm^{-1} , which corresponds to the in-plane C–C stretching vibration (ν_{19}) of benzene, was observed for all the doses of benzene applicable in this study. As in the cases of other bands, the intensity of this band grew progressively with the amount of benzene dosed. These data are included in Fig. 4(B).

Dose dependence of IR bands. Variation in the intensity of some of the above-mentioned vibrational bands is plotted in Fig. 8 as a function of benzene loading in HZSM-5. A progressive increase was observed in the intensity of all the vibrational bands (for instance, the 3039 and 1479 cm^{-1} bands shown as curves a and b in Fig. 8) for the range of benzene doses used in this study. The relative change in the intensity of ν_{19} and out-of-plane C–H vibrational bands is depicted in curve c of Fig. 8, which shows a typical plot of the intensity ratio of the 1479 and 3039 cm^{-1} bands.

Hydroxy region bands. The IR spectrum of HZSM-5, out-gassed at 625 K for ~ 20 h, showed the presence of three overlapping $\nu(\text{OH})$ bands at around 3745, 3670 and 3610 cm^{-1} , as shown in Fig. 9(A). Exposure at room temperature to benzene resulted in a gradual decrease in the intensity of these bands, accompanied by the appearance of two broad bands at around 3450 and 3300 cm^{-1} . The effect on individual bands depended on the amount of benzene dosed, as shown in Fig. 9(B). As the data in Fig. 9(B) are plotted with the spectrum of an activated but unexposed wafer as a reference, the IR bands showing negative absorbance (pointing downwards) indicate the removal of concerned species and those pointing upwards represent the new bands developed on adsorption of benzene. As seen in spectra a and b, the 3610 and 3670 cm^{-1} bands are

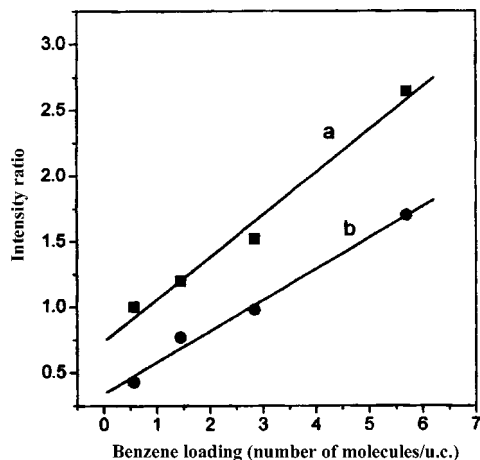


Fig. 7 Plots of the relative areas under different out-of-plane vibrations of benzene adsorbed in HZSM-5: (a) I_{1812}/I_{1850} and (b) I_{1957}/I_{1985} .

affected even at low exposures of benzene from 10 to 100 $\mu\text{mol g}^{-1}$. The species responsible for the 3746 cm^{-1} band is removed only for higher exposures of benzene (spectra c and d). The intensity of the $\nu(\text{OH})$ bands in the 3600–3750 cm^{-1}

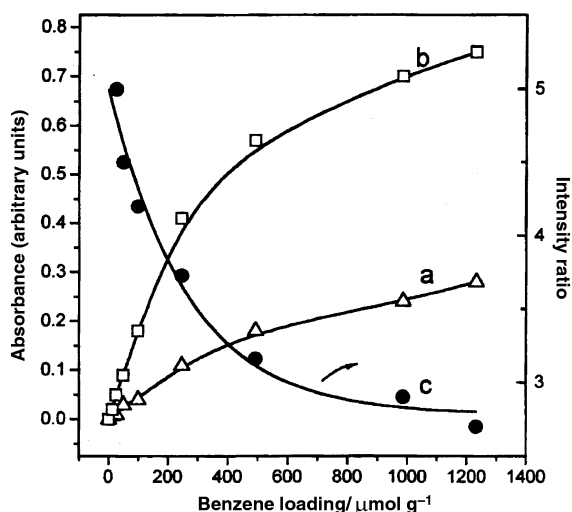


Fig. 8 Variation in intensity of some typical IR bands observed on HZSM-5 as a function of benzene loading at room temperature: (a) 3039 and (b) 1479 cm^{-1} . (c) Plot of intensity ratio I_{1479}/I_{3039} .

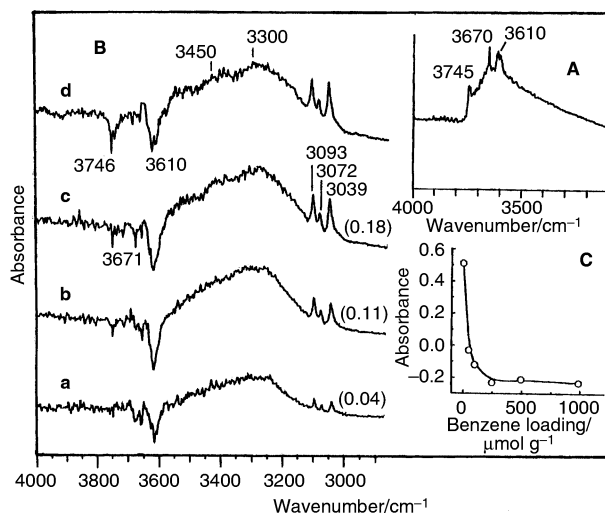


Fig. 9 Hydroxy region IR bands of HZSM-5 prior to (A) and after loading of different amounts of benzene (B). Benzene loadings: (a) 0.6, (b) 1.5, (c) 2.9 and (d) 5.7 molecules per unit cell. (C) Variation in intensity of 3610 cm^{-1} band as a function of benzene loading.

region and also those developed on benzene adsorption (Fig. 9(B)) reached saturation level for a loading of $\sim 200 \mu\text{mol g}^{-1}$ and no further changes were observed for higher loadings. The typical variation in the absorbance of the 3610 cm^{-1} band as a function of benzene loading is plotted in Fig. 9(C).

Discussion

As reviewed by Barthomeuf,²⁰ adsorption of benzene over silica and X and Y zeolites has been investigated by various workers.^{21–25} As in the case of the present study, the in-plane vibrations of adsorbed benzene are found to match with the frequencies of liquid phase benzene. The frequencies of out-of-plane IR bands are reported to exhibit a blue shift, the extent of which depended on the nature of the cation. Such observations have been interpreted earlier in terms of the specific interaction of the π -bonds of the benzene molecules with the electrostatic field associated with the charge balancing cations or alternately with the hydroxy acid sites of the zeolite framework. Thus, Barthomeuf *et al.*²⁴ reported a splitting of CH out-of-plane bands into two pairs on adsorption of benzene on zeolite β , where the low-frequency pair of bands is assigned to benzene interacting with cations through the π -cloud and the high-frequency pair of bands to weak interaction of CH with the framework oxygen. In a study on HEMT and NaEMT zeolites, Su *et al.*²⁵ reported multiple out-of-plane C–H stretching region vibrational bands accompanied by a red shift in the hydroxy region bands for adsorption of *ca.* 12.5 molecules per unit cell. These results have been interpreted in terms of an interaction of the π -cloud of the benzene ring with the zeolite hydroxy groups or with the charge balancing cations. Among the few IR studies reported on the adsorption of benzene over HZSM-5 or its corresponding cation-exchanged samples, we quote a recent work of Armaroli *et al.*²⁶ where the development of broad and weak $\nu(\text{OH})$ bands at 3250 and 3505 cm^{-1} observed on adsorption of benzene over HZSM-5 have been attributed to perturbation of bridging OH groups and terminal silanols.

Coming to the present study, the following are the salient features of IR spectra obtained for adsorption of benzene in HZSM-5 at room temperature.

(i) The frequencies of all the in-plane vibrations of adsorbed benzene as shown in Fig. 4 match closely with those of its liquid form (Table 1), and remain unaffected by benzene loading or on exchanging charge balancing cations in HZSM-5.

(ii) The intensity of the 1479 cm^{-1} band due to in-plane C–C stretching vibration (ν_{1g}) increases manifold on adsorption of benzene on zeolite, compared to the other higher frequency bands mentioned above. Thus while the intensity ratio of the 1479/3090 cm^{-1} bands in the case of standard liquid benzene spectrum was ~ 1.25 , this value in the case of adsorbed benzene was about 3.0. Similarly, the ratio of the 1479 and 3039 cm^{-1} bands in the case of liquid phase and in the adsorbed phase of benzene was 0.83 and 3.3, respectively (Fig. 8).

(iii) Spectra in Fig. 5 reveal a splitting of the combination C–H bending bands (1971 and 1833 cm^{-1}) for benzene loading above 1.6 molecules per unit cell. At least two pairs of bands are observed for each of these bands for benzene in its adsorbed form, the relative intensity depending upon loading and the nature of the charge compensating cation.

It is known that benzene has non-degenerate and doubly degenerate fundamentals and multiply degenerate combinations. In the gas phase or liquid state they appear as single bands. The splitting observed in the present study (Figs. 5 and 6) may have its origin in one or more of the following effects:

(a) Occupation of different sites: The benzene molecules may occupy different cavities, where they are held loosely and

are relatively free to rotate. Under these conditions, no degeneracy will be removed, and as many bands as there are types of cavities will be produced for all the fundamental and combination bands. However we see no splitting in infrared fundamentals at 3093 and 1480 cm^{-1} and in the in-plane combination vibrations at 3069 and 3037 cm^{-1} (Fig. 4). Furthermore, the widths of these un-split bands are not increased with loading (Fig. 4), providing no evidence for possible splitting. It is also difficult to envisage the existence of at least four different kinds of cavities in ZSM-5 where benzene molecules may reside simultaneously so as to give rise to distinct and multiple IR bands as seen in Fig. 5 for all the benzene loadings in the range 2 to 7 molecules per unit cell.

(b) Removal of D_{6h} symmetry: Benzene molecules trapped in narrow zeolitic channels may suffer distortion, resulting thereby in lowering of their D_{6h} symmetry and hence in changes in vibrational modes. For instance, lowering to C_{2v} symmetry will give rise to two bands in place of each active degenerate fundamental, one band in place of an inactive degenerate fundamental, and several bands for combinations and overtones. Such lowering of symmetry may also be envisaged for bonding of benzene molecules to framework or extra-framework sites of zeolites, such as cations and hydroxy groups. Band splitting under these circumstances may occur even for very low loadings. However, we may point out that the lowering of symmetry would result in shift or splitting (degenerate) of fundamental vibration also, particularly C–H stretching, which is contrary to our observation (Fig. 4). It is also important to note that the observed 6-fold rotation of adsorbed benzene molecules, as demonstrated clearly by QENS experiments, is not in harmony with this concept.

(c) Cluster formation: Formation of dimers or higher clusters of benzene in zeolitic pores will lead to an increased number of bands in infrared and Raman spectra. Any g (or u) modes from two molecules can be combined to give a g and u mode in a bimolecular cluster. Hence the mutual exclusion rule for the single molecules will be altered, and a u mode of a dimer, generated from the original g mode for the monomer, can become infrared active, and similarly for Raman bands.

We may point out that the shift of out-of-plane bands to frequencies higher than those of liquid phase benzene and their splitting by 10–15 cm^{-1} , as seen in Fig. 6, have been reported for the transition of benzene from liquid to solid state also.²⁷ Thus, while these bands appear at 1815 and 1959 cm^{-1} for liquid benzene, in the case of solid benzene they are observed in the form of doublets with new frequencies at around 1825, 1836 cm^{-1} and 1972, 1980 cm^{-1} , respectively.²⁸ The exact frequency of the bands depended on temperature.²⁸ It may be mentioned that no measurable frequency changes or splitting were observed for in-plane fundamental vibrations of benzene during such liquid \rightarrow solid transformations,^{27,28} as is also seen in Fig. 4. The IR data in Figs. 5 and 6 as a function of benzene loading thus provide a clue that the benzene adsorbed in zeolite may exist in a compressed (or clustered) state and this may happen for benzene loadings as low as $\sim 300 \mu\text{mol g}^{-1}$ (~ 1.6 molecules per unit cell). The change in intensity ratio of the fundamental vibration (ν_{1g}) at 1479 cm^{-1} and the other in-plane vibrations at 3092, 3071 and 3039 cm^{-1} (Fig. 8 curve c), as mentioned above, is also a feature accompanying the transition of liquid to the solid state of benzene.²⁸ The IR results of this study may thus be interpreted in terms of the formation of benzene clusters in zeolitic pores, as mentioned above. Clustering of benzene molecules may produce changes in IR spectra similar to those observed on compression or during liquid to solid phase transformations.

As discussed elsewhere in detail,²⁹ clustering of benzene molecules inside zeolitic pores may be envisaged to occur if they are packed one by the side of another and with their planes parallel to the walls of the zeolitic channels. In this

mode of packing, benzene molecules will experience immense π – π bond interaction, resulting in splitting of out-of-plane C–H vibrations. Such a stacking of benzene molecules will also lead to compression of C–H bonds, to an increase in the effective force constants and hence to an upward shift in frequency of split out-of-plane C–H vibrational bands, as is actually seen in spectra of Fig. 5. The corresponding perturbation of in-plane vibrational modes will be rather small, resulting in only marginal frequency changes, if any. Though we observed no measurable changes in the frequency of fundamental vibrational bands on benzene adsorption, Huang and Hwang³⁰ have recently reported a splitting into two of the Raman active fundamental bands of liquid benzene on adsorption in siliceous ZSM-5 zeolite. Also, a localized clustering in this mode may occur even for low loadings of benzene (< 3 molecules/u.c.), in agreement with the data in Fig. 6. We may also suggest that the changes in the relative intensity of the two different pairs of out-of-plane C–H vibrational bands, as shown in Figs. 6 and 7, and also as a function of cation exchange (Fig. 5), reveal the existence of at least two different types of pores having different sizes and volumes where the number of molecular clusters accommodated may differ. An obvious identity of these pores could be the straight channels and their intersections. These aspects are discussed elsewhere in detail.²⁹

The concept of cluster formation is in harmony with the quasi-elastic neutron scattering studies showing that the translational motion of benzene adsorbed in zeolite pores is too slow and the encapsulated benzene molecules undergo a 6-fold rotation. This suggests a localized state of benzene in zeolitic pores, with no electronic bonding with cationic sites, thus enabling a 6-fold rotation. This is in further agreement with the reported calorimetric^{31,32} and NMR³³ data, suggesting that up to four benzene molecules per unit cell are localized at room temperature in the channel intersections in ZSM-5. In the powder neutron and X-ray diffraction studies reported on faujasite zeolites,^{34,35} it has been found that the benzene molecules are largely localized in the supercages at a temperature of 4 K giving rise to the formation of their clusters at higher loading. At room temperature the benzene molecules are found to be confined in the supercages, though no fixed coordinates are envisaged thus suggesting their delocalization. This difference with respect to the observations of the present study could be attributed to the large pore size (~ 1.2 nm) of X or Y zeolite compared to ~ 0.5 nm size of ZSM-5 channels.

The observed residence time of 16.5 ps for the benzene entrapped in zeolitic cages, compared to reported times of ~ 2.5 ps in the case of the liquid state³⁶ and 19.2 ps for its solid state³⁷ at 277 K, confirms again the existence of densely packed benzene molecules within the zeolitic cages. Earlier studies^{38,39} have similarly reported a 6-fold rotation of benzene molecules in ZSM-5 zeolite at room temperature, though deviations of EISF from the 6-fold model at lower temperature were observed. However, the residence time observed in our study is higher compared to that reported by Jobic *et al.*³⁸ suggesting that the packing of benzene may depend on certain factors such as sample characteristics, the details of which cannot be predicted at present.

As seen in Fig. 9, the removal of IR bands at 3671 and 3610 cm^{-1} (due to hydroxy groups located in the main channels and identified with Al–OH groups in defective extra-lattice positions and bridging structural hydroxy groups responsible for Brønsted acidity, respectively), even at low loading ($< 10 \mu\text{mol g}^{-1}$) of benzene, indicates that the benzene molecules initially occupy the main channels or their intersections, while the external silanols (3746 cm^{-1} band) are influenced only at higher exposures. The disappearance of hydroxy bands on adsorption of benzene in zeolites and their bathochromic shift has been attributed earlier to the perturbation of the surface

hydroxy groups due to interaction with the π -bonds of benzene molecules. We would like to thank the referee for suggesting that this kind of interaction with specific zeolitic sites may occur at the initial stages of benzene adsorption, and the cluster formation could take place between these bonded species and the further incoming molecules. The data in Fig. 9(C) tend to support this viewpoint where a saturation intensity of internal $\nu(\text{OH})$ bands at 3671 and 3610 cm^{-1} is observed at a loading of as low as 1.5 molecules per unit cell. It is thus likely that the initial binding of C_6H_6 molecules at OH or at other framework sites may assist in the process of cluster formation. However, once a benzene cluster is formed it may not remain bound to a particular site, as is evident from their 6-fold rotation observed in QENS results. Furthermore, the binding of individual benzene molecules by hydrogen bonding with zeolite sites is expected to result in significant changes in the frequencies of in-plane (especially C–H stretching) vibrations of adsorbed benzene also, which is contrary to our observations (Fig. 5). We may also point out that the average width at half-maximum of the shifted bands (3500–3200 cm^{-1} region) is larger by at least a factor of 6 compared to the corresponding un-shifted $\nu(\text{OH})$ bands in the 3800–3600 cm^{-1} region (Fig. 9B). It is therefore likely that the benzene clusters, packed in zeolitic cages in a mode as discussed above, may cause perturbation of acidic hydroxy groups by an additional process, other than direct electronic binding. Further work is being undertaken up to further understand this phenomenon.

Conclusions

In conclusion, our results point to an important role played by the shape and the size of zeolitic channels in encapsulation of small molecules. The benzene molecules occluded in zeolite cages experience an immense pressure effect, leading thereby to strong benzene–benzene intermolecular interaction and giving rise eventually to a clustered state of benzene, depending on its amount adsorbed. Even though the electronic bonding of benzene molecules with either the framework hydroxy groups or the charge balancing cations of zeolites may be important for initiation of this process, the molecular clusters once formed are free to rotate inside the channels. Data in Fig. 8 show that the intensity of certain unperturbed fundamental vibrations of benzene changes monotonically with loading and also with the change in charge balancing cation and hence pore size. The intensity of these IR bands may therefore serve as a means of evaluating pore size/pore volumes in such microporous zeolites and for detection of subtle changes as a function of cation exchange or other structural modifications.

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