Benzene in Hydrogen Zeolites

Infrared Spectroscopic and Catalytic Investigation of Variously Exchanged Hydrogen Y Systems

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Received 22nd December, 1980

Infrared spectra of sorbed benzene on several hydrogen Y zeolites, where the extent of proton exchange varied from 0 to 100%, are reported together with catalytic data for the ethylation of benzene over the same samples. Shifts of the zeolite hydroxyl band at 3640 cm⁻¹ to lower frequencies with increasing proton content are considered. A study of the out-of-plane C—H vibrations indicates an abrupt change in the strength of the benzene–surface bond at *ca*. 35 protons per unit cell; below this level of exchange the benzene is more tightly bound. The activity of the catalysts in the ethylation of benzene with ethanol is discussed; tightly held benzene at low levels of proton exchange is likely to reduce observed rates through hindered diffusion whereas for proton contents > 35 per unit cell the absence of hindered diffusion allows an exponential-type increase in alkylation rate, due to increased acidity, to be fully manifested. The paper shows how zeolitic cations can limit catalysis by localizing reactant or product molecules which in turn render the catalysis diffusion controlled.

One of the more important goals yet to be achieved in studies of catalytic conversions over zeolites is the detailed understanding of the reaction pathways which various molecules undergo. This information is vital in order that new and more specific catalysts may be developed. To this end many of the investigative techniques of surface science have found application in catalysis, none more so than that of infrared spectroscopy.¹⁻³ This technique allows the study of not only the nature of the active sites on the catalyst surface, but also the interactions of the reactant and product molecules with these active centres.⁴⁻⁶ In this respect the interactions of sorbed molecules with OH groups⁷ and with zeolitic cations^{8, 9} are of primary importance.

In this paper we describe the interactions of benzene with the surface of a range of NaHY zeolites; while to date some workers have at one extreme studied the interaction of benzene with parent NaY and at the other extreme with highly exchanged NaHY, no previous attempt has been made to detail the changes that occur in the spectra of adsorbed benzene molecules as the proton content of the zeolites is increased from 0 to 100%. On the catalysis side these materials have received some attention and their peculiar activity in isomerization and alkylation reactions has been noted.¹⁰⁻¹² The present paper also discusses the activity of the NaHY samples in the ethylation of benzene with ethanol and an attempt is made to correlate the activity profile obtained with our i.r. data. Spectra of sorbed benzene on CeY and LaY zeolites are also reported and discussed; these highly exchanged multivalent cationic samples have little sodium in their supercages and are very useful for comparison purposes where deductions regarding the effect of sodium cations on the catalysis are being made.

EXPERIMENTAL

The unit-cell compositions of the exchanged zeolites used in this study are presented in table 1, where the values in column 1 refer to the % exchange. The low-exchange samples were prepared by conventional ion exchange using NH₄Cl at room temperature. For exchange levels in the range 70-100% the zeolites were treated under reflux conditions with concentrated NH₄Cl solutions for several weeks. The rare earth catalysts CeY and LaY were first ion exchanged at room temperature with the nitrate salt and then refluxed for a number of days to achieve higher levels of exchange. The crystallinity of the samples was verified using X-ray diffraction.

zeolite	Na ⁺ per unit cell	NH ₄ ⁺ per unit cell	M^{n+} per unit cell
NaY	58.0		
NaNH ₄ Y-31	40.0	18.0	
NaNH ₄ Y-46	31.0	27.0	_
NaNH ₄ Y-60	23.0	35.0	
NaNH ₄ Y-72	16.0	42.0	
NaNH ₄ Y-78	12.5	45.5	_
NH₄Y		58.0	<u> </u>
CeY	5.5	_	17.5
LaY	4.0		18.0

TABLE. 1.—CHEMICAL COMPOSITION OF ZEOLITES BEFORE CALCINATION

The benzene used was AnalaR research grade which was further dried and stored over an activated molecular sieve. The i.r. spectra were recorded on a Perkin-Elmer type 377 spectrophotometer. The zeolite samples were compressed into small discs which were then outgassed at 673 K and a pressure of 10^{-5} mmHg for a period of 24 h in a portable i.r. cell.¹³ The sorption of benzene was performed at 423 K. Before recording the spectra the excess vapour in the cell was removed by outgassing at the temperature of sorption. All spectra were recorded at room temperature with a resolution of 4 cm⁻¹. The catalytic apparatus and operating mode was similar to that described previously.¹⁴⁻¹⁷

RESULTS

Two OH bands are present in the i.r. spectra of NaHY zeolites shown in fig. 1(a)-(d): the high-frequency (h.f.) band at 3640 cm⁻¹ and the low-frequency (l.f.) band at 3540 cm⁻¹. The spectra of sorbed benzene on some of the catalysts studied as well as that for liquid benzene are presented in fig. 2 and 3. The assignments of the principal vibrational bands of benzene observed in both the liquid and gaseous phase and after adsorption on the catalysts are given in table 2. As would be expected, strong perturbations of the OH groups occur on adsorption of benzene; the spectra also indicate significant changes in the spectra of sorbed benzene over the range of NaHY samples studied.

For the 100% exchange HY sample, fig. 2(b), the h.f. hydroxyl band at 3640 cm⁻¹ in the dehydrated zeolite, *cf.* fig. 1(a), is shifted to a lower wavenumber $(\Delta \bar{\nu} \approx 300 \text{ cm}^{-1})$ and the band is considerably broadened and increased in intensity relative to the original band at 3540 cm⁻¹, which is not shifted. The spectrum of the sorbed benzene on this sample also indicates that the bands at 1815 and 1960 cm⁻¹ in the liquid-phase spectrum, fig. 2(a), are shifted to 1837 and 1975 cm⁻¹, respectively, and are broadened considerably. In comparison with the spectrum of liquid benzene these bands are also considerably increased in intensity relative to the bands at 3040, 3070 and 3090 cm⁻¹. For NaHY-78 the spectrum obtained after adsorption of benzene was very similar to that for the 100% exchanged sample, except for a smaller band shift in the h.f. hydroxyl group and a less pronounced increase also in the intensity and broadening of the bands at 1837 and 1975 cm⁻¹. For NaHY-60, fig. 2(c), there



FIG. 1.—Low- and high-frequency hydroxyl bands in (a) HY, (b) NaHY-60, (c) NaHY-46 and (d) CeY.

is again a comparable band broadening and also a band shift to even higher frequencies of the 1815 and 1960 cm⁻¹ liquid benzene bands. For the sample NaNH₄Y-46, fig. 3(*a*), the h.f. hydroxyl band is shifted only slightly to 3600 cm⁻¹ although a broad absorption is observed in the region 3500-3200 cm⁻¹. A more important observation however with regard to the spectrum for this sample centres on the region 2050-1800 cm⁻¹, where instead of two broad bands as observed in the spectra of the previous samples, the bands are split to give a doublet structure, *i.e.* bands at 1880, 1850, 2020 and 1987 cm⁻¹. This doublet structure was also observed for the higher sodium content samples NaHY-31 and NaY, fig. 3(*b*); furthermore, for benzene sorbed on samples NaHY-46, NaHY-31 and NaY there is a noticeable splitting of the benzene bands at 3090, 3070 and 3040 cm⁻¹ which is not observed for the higher exchange samples. For benzene sorbed on the rare earth zeolites LaY and CeY, fig. 3(*c*) and table 2, it can be seen that after pumping at the temperature at which the benzene bands are of very

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weak intensity and are virtually unobservable in the region 2050-1800 cm⁻¹ except on expansion of the transmission axis.

DISCUSSION

A broadening and shift to lower frequencies of the h.f. hydroxyl group in NaHY zeolites has also been observed by previous workers on adsorption of alkanes²⁰ and rare gases,²¹ the shift being smaller, in the region of 100 cm⁻¹ for alkanes and lower



FIG. 2.—Comparison of spectra of (a) liquid benzene with sorbed benzene on (b) HY and (c) $NaNH_4Y-60$.

again for the rare gases. This broadening and shift to lower frequency can be attributed to electrostatic interactions of the OH dipole with neighbouring molecules, which results in the displacement of the electrical change in these molecules and, as a consequence, in the increase of the dipole moment as well as a descrease of the force constant of the OH bond. The increased shift relative to the alkanes for benzene sorbed on the 100% exchanged sample can be attributed in the main to the larger polarisability of the aromatic ring. The smaller shifts ($\Delta \bar{\nu} \approx 40 \text{ cm}^{-1}$) observed for the low-exchange samples indicates that the nature of the interactions with the OH groups varies quite considerably with the extent of ammonium exchange. The broadening of the bands in the region $2050-1800 \text{ cm}^{-1}$ and the shift in frequencies observed would suggest that these are the bands which are mainly affected by adsorption of benzene on the OH groups or charge-balancing cations. In order to see more clearly the nature of the interaction of benzene with the zeolite structure, the transmission axis was expanded (\times 5) in the region 2050-1800 cm⁻¹, fig. 4. The bands in this region result from combinations of the out-of-plane C—H bending



FIG. 3.—Infrared spectra of benzene sorbed on (a) NaHY-46, (b) NaY and (c) CeY.

vibrations of the benzene molecule.²² These trends in the i.r. data parallel those observed by previous workers⁸ and lend support to an adsorption mechanism which weakens the π -electron bonds of the aromatic ring while simultaneously locking the ring into a fixed configuration relative to the surface; this configuration does not favour out-of-plane vibrations. The greater the interaction of the adsorbed molecule with the zeolite surface, the greater will be the alteration in the force constant of the C—H bond and fluctuating dipole and consequently the more difficult it will be for these out-of-plane vibrations to occur; as a consequence the bands associated with these vibrations should appear at higher frequencies and with greater intensities. As indicated in fig. 4 and table 2, progression from low to high sodium content zeolites results in the shift of these bands to a higher frequency; this effect is shown clearly

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TABLE 2.—INFRARED DATA FOR SORBED BENZENE

vibration mode ^a	attribution ^b	gaseous	liquid	ΗΥ	NaHY-78	NaHY-72	NaHY-60	NaHY-46	NaHY-31	NaY	LaY, CeY
v ₂₀ v1	C—H stretching C—C stretching	3090	3090	3090	3090	3090	3090	3909¢	3090°	3090°	3090 (v.w.)
+ 2° + 2°	CC stretching + CC-C//bending	3073	3070	3070	3070	3070	3070	3070°	3070°	3070°	3070 (v.w.)
¹ 19	C-C stretching +	3045	3047	3040	3040	3040	3040	3040^{c}	3040^{c}	3040^{c}	3040 (v.w.)
ا _ت د م	C-C succound C-H bending L	1964	1960	1975	1975	1975	1987	2020 +	2020 +	2020	
- ^V 1, 10	C—H bending ⊥ C—H bending ⊥ ⊥	1807	1815	1837	1837	1837	1880 (v.w.) 	1987 1880	1987 1880 +	1987 1880	
V ₁₇ V ₁₉	C—H bending ⊥ C—C stretching	1485	1478	1480	1480	1480	1847 1480	1847 1480	1847 1480	1847 1480	1480 (v.w.)
			a Ref. (18);	⁵ ref. (19);	° slight sp	litting.				

in fig. 5, which is a plot of the observed frequency against the proton content per unit cell for all of the samples studied. The most notable feature in this plot is the abrupt frequency drop at a H^+ content of between 35 and 42 per unit cell, which coincides with a complete removal of sodium ions from the large cavity of the zeolite. A further point of interest, clearly visible in fig. 4, is the splitting of the bands for the low-exchange



FIG. 4.—Comparison of i.r. bands of sorbed benzene on (a) NaY, (b) NaHY-31, (c) NaHY-60 and (d) NaHY-78.

samples. This splitting has also been observed by Primet *et al.*⁹ for benzene sorbed on NaY. Thus it seems evident from the above results that the presence of Na⁺ ions in the supercage is responsible for the increase in the vibration frequency of the C—H out-of-plane vibrations together with the splitting of these bands. This is indicative of a strong interaction of benzene with Na⁺ ions most probably in site II positions. For sorption of benzene on NaX zeolites, very little perturbation of these out-of-plane vibrations is observed, which may be accounted for by the much larger electric fields associated with the site II position in Y-type zeolites²³ as compared with the more siliceous X zeolites. N.m.r.²⁴ results too indicate a strong interaction of benzene with the surface of NaY zeolite.



FIG. 5.-Spectral variation of benzene bands with extent of ammonium exchange.

In samples which contain more than 35 H⁺ ions per unit cell the doublet structure is not evident, fig. 4(c) and (d); instead a broad band with decreased frequency is observed, the degree of broadening increasing with the proton content, being most pronounced for the 100% exchanged sample. Thus a different mechanism of adsorption must be assumed on protonic sites. The following equation



represents the equilibrium which is set up on the catalyst surface on introduction of H^+ ions. The left-hand side of eqn (I) represents a classical Brønsted acid site. However Uytterhoeven et al.²⁵ have noted that this species is not present in substantial quantities at low temperature. Protons can be supplied through the equilibrium of eqn (I) on the introduction of a base. As a direct measure of this equilibrium, proton jump frequencies have been calculated and it was found that the jump frequency on adsorption of benzene was much smaller than that calculated for adsorption of the stronger base pyridine.²⁶ Thus on adsorption of benzene on these highly exchanged samples, the interaction would seem to be weak and non-specific, particularly at low temperatures. Here the interaction is mainly with OH groups, giving hydrogenbond-type interaction, similar to that postulated by Angell et al.²⁷ for adsorption of acetonitrile on a HY catalyst. The decreased interaction of a π -electron system with highly exchanged NaHY zeolites has also been observed by Galuska et al.²⁸ for but-1-ene adsorption. They observed that on removal of Na⁺ ions from accessible positions, but-1-ene consumption (which they have shown to be due to interaction of the π electrons with Na⁺ ions²⁹) is decreased dramatically indicating a low affinity of the hydroxyl groups for the π -electron system. The non-specific nature of the

adsorption interaction for benzene sorbed onto these highly exchanged NaHY samples is further corroborated by n.m.r. data³⁰ which indicate a highly mobile phase for benzene sorbed on similar samples. In contrast to this weak and non-specific type of interaction observed for the low sodium content zeolites, samples which contain appreciable amounts of sodium exhibit much sharper and more specific bands in the region 2050-1800 cm⁻¹ indicating a much stronger electrostatic interaction of benzene with the Na⁺ ions.

As indicated previously, the bands in the region 2050-1800 cm⁻¹ due to out-of-plane vibration are almost unobservable for benzene sorbed on LaY and CeY. Furthermore, the intensity of the 1485 cm⁻¹ band, fig. 3(c), is also very weak, which seems to indicate that almost all the benzene is desorbed by pumping at the temperature of sorption. N.m.r.²⁴ data also indicate highly mobile benzene molecules sorbed on similar samples. Ion exchange of Ce³⁺ and La³⁺ ions into NaY has been shown²⁷ to lead to almost complete removal of ions from supercage positions, which clearly leads to interaction of a non-specific nature for molecules adsorbed on these samples, in keeping with the present observations.



FIG. 6.—Ethylation of benzene with ethanol at 423 K in the steady state in equimolar mixture of toluene and benzene as a function of unit cell proton content; the rates are expressed with respect to ethylbenzene formed.

The catalytic activity of the NaHY samples for the ethylation of benzene using ethanol as the ethylating agent are presented in fig. 6 as a function of the proton content (H⁺ per unit cell). The rates of ethylation are seen to increase fairly linearly from 16 up to *ca*. 28 H⁺ per unit cell and then as the remaining Na⁺ ions are replaced the rates show an accelerating increase. Ethylation of the aromatic is generally believed to proceed *via* a Rideal-type mechanism³¹ involving adsorption of ethanol on an active site (—OH group) to form a carbonium ion species, which is then attacked by the free or very weakly held aromatic molecule. Clearly any factor which would alter the diffusion of reactants to, or products away from, the locus of catalytic activity would also alter the rate of the reaction. In the present circumstances strong binding of the aromatic to Na⁺ ions in the supercage must surely be an important factor when hindered diffusion is being considered.

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As has been indicated in fig. 5 removal of all the Na⁺ ions from supercage positions in these catalysts leads to benzene molecules of a much more mobile nature as evidenced by the abrupt frequency changes. While the Brønsted acidity and the changes thereof which occur on increasing degree of exchange³² may account for the increased rate of ethylation above approximately 40 H⁺ ions per unit cell, the absence of strongly held immobile benzene, which in higher sodium content samples reduces the alkylation rate by hindering diffusion of reactants to, and products from, the active site, must also play a significant part. We have observed the catalytic activity of the rare earth exchanged samples for this reaction to be many times greater than expected on the basis of the number of acid sites present; while this again may be attributed

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into zeolite	T/K	NaY	HY-75	HY-97.7
1,3,5-trimethylbenzene	273	13.0	> 100	_
1,3,5-tri-isopropylbenzene	303	0.047	3.2	9.3
1,3,5-tri-isopropylcyclohexane	303	4.9	3.2	8.7

Fable 3.—Unidirectional	DIFFUSION OF	HYDROCARBONS	INTO	THE Y	ZEOLITE
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to increased acidity due to the high polarizing ability of the multivalent cation, the absence of strongly held benzene, fig. 3(c), must also be important. The specific interaction of molecules containing π electrons with zeolitic sodium cations and its marked effect on the molecular diffusion coefficient is underlined by the data^{33, 34} of table 3: 1,3,5-tri-isopropylcyclohexane even though slightly larger than 1,3,5-tri-isopropylbenzene diffuses faster in NaY; its rate does not vary much between the NaY and HY samples; however, the rate of diffusion of both 1,3,5-trimethylbenzene and 1,3,5-tri-isopropylbenzene increased dramatically in going from NaY to HY.

CONCLUSION

An i.r. study of sorbed benzene in hydrogen Y zeolites of various degrees of proton exchange, from 0 to 100%, shows that the benzene is held relatively tightly by sodium cations in samples with degrees of exchange corresponding to less than 35 H⁺ ions per unit cell. These immobilized benzene molecules render catalysis in the ethylation of benzene to be diffusion controlled. The spectroscopic measurements also show that in samples exchanged to degrees corresponding to 35-58 H⁺ per unit cell the benzene molecules are more mobile and do not impose a restriction of diffusion-controlled catalysis. These samples are also more acidic and there is a corresponding exponentialtype increase in the rate of ethylation of benzene over these catalysts. Thus it is established that increasing the number of supercage cations increases the possibility that diffusion effects will be observed in catalysis.

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(PAPER 0/1969)