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Adsorption of Benzene and Benzene Derivatives onto Zeolite H-Y Studied by Microcalorimetry

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Differential enthalpies of adsorption (ΔH_{ads}) of benzene, ethylbenzene, and 1,3- and 1,4-diethylbenzene onto zeolite H-Y at 323 K were measured as a function of sorbate coverage using a microcalorimeter of the Tian–Calvet type. The ΔH_{ads} values which correspond to interaction with acidic Brønsted sites varied between the various probe molecules in the range 66 to 125 kJ mol⁻¹ (neglecting the initial high enthalpies) and increased in the following order: benzene < ethylbenzene < 1,4-diethylbenzene \approx 1,3-diethylbenzene. Benzene exhibited a constant ΔH_{ads} over a wide range of sorbate loadings, while the substituted benzenes showed gradual increases in ΔH_{ads} with coverage, indicating mutual interaction between sorbate molecules. The total number of molecules which were adsorbed per unit mass of zeolite varied inversely with the size of the sorbate molecule, in accordance with volumetric limitations. High values of ΔH_{ads} were evolved on sorbing the first few molecules of any of the sorbates per unit cell, due to the interaction between the sorbate and small numbers of residual Na⁺ cations in the zeolite. The differential heats of adsorption of 1,4-diethylbenzene onto dehydroxylated H-Y, as well as partially sodium-exchanged H-Y, were measured for comparison.

Introduction

The interaction of gases or vapors with solid surfaces is a fundamental process which is utilized in countless practical applications. The energy of interaction is often small, and thus a precise, highly sensitive technique is needed to accurately measure the enthalpies of interaction. An accurate measure of the acidity or basicity of a catalyst is essential to allow comparison between catalysts prepared by different methods. Certain reactions may require strongly acidic or basic catalysts, while others may even occur over catalysts of intermediate strength. Protonation of aromatics² and skeletal isomerization of alkanes³ require strongly acidic catalysts, while the migration of double bonds in alkenes⁴ is favored over relatively weaker acid sites. Dehydrogenation reactions, on the other hand, proceed in the presence of basic catalysts.⁵ The relative acidity or basicity of a catalyst may be determined by measuring the enthalpy of interaction between a basic or acidic gas, respectively, with these catalytic sites. Although this does not provide an *absolute* scale of acidity/basicity, it enables a ranking of the acidic or basic properties of zeolites of a homologous series. Microcalorimetry is the only direct method to measure such enthalpies and was used in this study to investigate the interaction of ethylbenzene and the products from its disproportionation (benzene and the diethylbenzenes), with a solid zeolite H-Y catalyst.

The disproportionation of ethylbenzene over acidic zeolites has been proposed by Karge et al.^{6–8} as a suitable

test for the acidity of the catalysts. When properly conducted, the reaction is 100% selective toward benzene and diethylbenzenes and yields no unsaturated polymerizable species; thus, deactivation of the catalyst due to, e.g., polymerization or coke formation, does not occur. The reaction has been shown to be catalyzed only by zeolites possessing strong Brønsted sites, of $H_0 \leq -8.2$ (acidity according to titration against Hammett indicators).⁷ Under certain conditions, however, reversible inhibition of the disproportionation reaction has been observed to occur when using H-Y zeolite as the catalyst.^{9,10} When a small quantity of diethylbenzene was introduced into the feed stream of an ethylbenzene disproportionation reaction which was at steady state, the yield of benzene immediately dropped and remained at a reduced level. The yield of diethylbenzene initially artificially increased due to its addition to the feed but then decreased again as strong adsorption onto the catalyst occurred. When the diethylbenzene was removed from the feed stream, the yields of benzene and diethylbenzene returned gradually to their earlier steady-state values. This effect was proposed to be due to preferential adsorption of the produced diethylbenzenes onto the zeolite. One aim of the work reported here is to confirm this assumption via microcalorimetric measurements of the differential enthalpies of adsorption onto H-Y zeolite of ethylbenzene and the products of ethylbenzene disproportionation. While there exist in the literature several data on the sorption enthalpies of benzene, *p*-xylene, etc., into zeolites, the present article is the first to report a comparative study of the differential enthalpies of adsorption of benzene, ethylbenzene, and 1,3- and 1,4-diethylbenzene determined by microcalorimetry.

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Table 1. Summary of Calorimetric Results^a

sample	adsorbate	$\Delta H_{\text{ads-init}}/\text{kJ mol}^{-1}$	strongly ads/molec (u.c.) ⁻¹	$\Delta H_{\text{ads-intermed}}/\text{kJ mol}^{-1}$	saturation coverage/molec (u.c.) ⁻¹
H-Y	benzene	75–95 \pm 5	1–3	66–67 \pm 3	37.5
H-Y	ethylbenzene	70–75 \pm 4	1	65–105 \pm 5	30
H-Y	1,3-diethylbenzene	140 \pm 7	4–5	107–126 \pm 6	21
H-Y	1,4-diethylbenzene	120–170 \pm 8	2–5	107–122 \pm 6	20
Na _{0.7} H-Y	1,4-diethylbenzene	180 \pm 9	8–10	114–121 \pm 6	22
H-Y _{De-OH}	1,4-diethylbenzene	140 \pm 7		95–112 \pm 5	13

^a Definitions: $\Delta H_{\text{ads-init}}$ = approximate initial ΔH_{ads} ; strongly ads = number of molecules/u.c. adsorbed before plateau or steadily rising portion of curve; $\Delta H_{\text{ads-intermed}}$ = ΔH_{ads} during plateau or steadily-rising portion of curve.

Experimental Section

All samples studied here were derived from the same batch of zeolite Na–Y supplied by the late Dr. W. O. Haag of Mobil Corp., Princeton, NJ. Zeolite NH₄-Y was prepared by ion exchange of Na–Y and possessed the composition (NH₄)_{54.6}Na_{0.25}Al_{55.1}Si₁₃₇O₃₈₄·205H₂O (Si/Al = 2.49), as determined from atomic absorption spectrophotometry and combined thermogravimetric and gas-chromatographic analyses.

To prepare the sample for the microcalorimetric measurements, the zeolite powder was lightly pressed into a disk of thickness ca. 0.1 mm and then cut into small platelets (<1 mm square). These were then sieved to remove residual zeolite powder and larger platelets. The zeolite was used in the form of platelets in order to avoid loss of powder when the cell was evacuated. Approximately 50–100 mg was introduced into the calorimetric sample cell, the design of which is described elsewhere.¹¹ The sample cell was then placed under dynamic vacuum overnight before initiating the following temperature program to facilitate activation. From ambient, the temperature was raised at 5 K min⁻¹ to 453 K and was kept there for 2 h to facilitate dehydration. The temperature was then raised to 673 K at 1 K min⁻¹ and was kept there for 4 h to remove NH₃, any residual water, and other adsorbates, followed by cooling at 5 K min⁻¹ to 323 K. Once the temperature program came to an end, the cell was sealed while still under dynamic vacuum by means of a high-vacuum valve, was transferred to the microcalorimeter (also at 323 K), and was attached to the volumetric system for gas adsorption. The volumetric system was then evacuated and baked-out, with the calorimetric cell isolated by the vacuum valve to avoid contamination of the sample. Samples prepared in such a way are referred to as H-Y throughout this work.

A sample was prepared such that the number of residual Na⁺/u.c. (unit cell) was slightly larger than that in the H-Y described above. The sample was prepared via ion exchange from the parent Na-Y. This sample was found to contain approximately 0.7 residual Na⁺/u.c. and is referred to as Na_{0.7}H-Y.

Sample Na_{0.7}H-Y was used as the starting material to prepare a dehydroxylated material. Dehydroxylation results in the generation of Lewis acidity by extracting aluminum species from the zeolite framework. Dehydroxylation was performed in a quartz-glass vacuum chamber using small platelets of zeolite, pressed and sieved as described above. From ambient, the temperature was raised at 5 K min⁻¹ to 453 K and was kept there for 2 h to remove water. The temperature was then raised to 873 K at 1 K min⁻¹ and was kept there for 4 h, followed by cooling at 5 K min⁻¹ to ambient. The sample was then transferred to the microcalorimetric cell, which necessitated brief exposure to air. The sample was then reactivated at 673 K, as described earlier, before moving the sealed cell to the microcalorimeter. Reactivation was necessary as the zeolite readily picks up water and other adsorbates on exposure to air. The dehydroxylated and reactivated sample is referred to as H-Y_{De-OH} throughout the text.

Benzene and its ethylated derivatives were purified immediately prior to use by passing them over activated alumina at room temperature to remove oxidation products. Once introduced into the calorimeter's volumetric system, the sorbates were further purified by a minimum of three freeze–pump–thaw cycles. The time between purification over activated alumina and performing the freeze–pump–thaw cycles was kept to an absolute minimum, and exposure to air and light was avoided throughout the experiments to prevent oxidation or degradation.

It was found necessary to store ethylbenzene over activated alumina in the gas preparation portion of the microcalorimeter's volumetric system in order to obtain reproducible results for this sorbate.

The microcalorimetric sample cells,¹¹ volumetric apparatus,¹² and procedure for determining differential enthalpy of adsorption versus coverage¹² have been described elsewhere.

Thermogravimetric analyses were performed using a Perkin-Elmer TGS-2 thermobalance under high vacuum, which was linked to a gas chromatograph for identification of desorbing species.

Atomic absorption spectrophotometric results were obtained using a Perkin-Elmer 4100 spectrophotometer. Solid zeolite samples were dissolved in an aqueous solution of HF in a Teflon-lined digestion bomb at elevated temperature prior to analysis.

Infrared spectra were recorded with a Perkin-Elmer PE 225 spectrometer. Self-supporting wafers of the zeolite were pressed and mounted in a high-vacuum quartz IR cell.¹³ The samples were activated *in situ* to 673 K following a temperature profile similar to that described above. Spectra of the activated zeolite prior to, and following, adsorption of pyridine were recorded at the temperature generated by the IR beam (approximately 353–373 K). Pyridine is known to interact with both Brønsted and Lewis acid sites in zeolites and is frequently used as a probe for these sites.

Results and Discussion

To allow easy comparison between figures, all calorimetric data are plotted with the same *x*- and *y*-axis scales. Table 1 summarizes the calorimetric results obtained.

Plots of ΔH_{ads} versus adsorbate coverage for the adsorption of benzene onto H-Y are shown in Figure 1. The results are reproducible, as shown by the coincidence of two sets of data, measured under identical conditions using separately prepared H-Y samples. Adsorption of the first molecule or two per unit cell onto the sample generates relatively high differential heats and may be associated with the interaction between benzene and extraframework metal cations (Na⁺); *vide infra*. Thereafter, the ΔH_{ads} remains constant at about 67 kJ mol⁻¹ over a wide range of coverages as the Brønsted acid sites are titrated, until approximately 27 molecules have been adsorbed per u.c. A continuous drop in ΔH_{ads} (due to a distribution of site strength) marks the saturation of the pore volume as the differential heats evolved drop to those associated with physisorption on the surface of the crystals at a benzene coverage of 35–40 molecules/u.c. From the composition of the framework, one could expect 55 adsorption sites/u.c. (i.e., 55 Al atoms/u.c.); geometrical constraints (inaccessibility of sites in the β -cages¹⁴) probably account for the lower benzene coverage determined experimentally. Calculation shows that up to 44 benzene molecules may be accommodated in the supercages of the faujasite structure; see Table 2. The constancy

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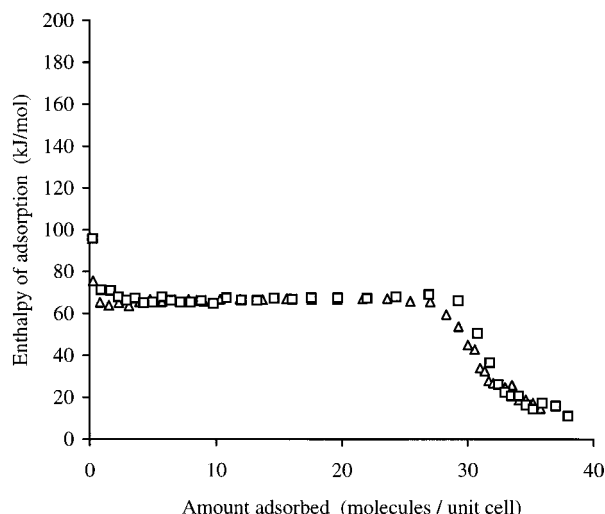


Figure 1. Enthalpy of adsorption of benzene onto H-Y versus sorbate coverage at 323 K. Two sets of data were measured under identical conditions.

Table 2. Adsorbate Volumes and Calculated Maximum Achievable Coverages on Zeolite H-Y

adsorbate	molecular vol ^a /nm ³	calcd max coverage ^b /molec (u.c.) ⁻¹
benzene	0.148	44
ethylbenzene	0.203	32
1,4-diethylbenzene	0.258 ₆	25
1,3-diethylbenzene	0.259 ₁	25

^a Calculated for the liquid at 298 K from molecular weight and density. ^b Based on calculated volume of supercage = 0.822 nm³ (ignoring cations) and assuming β -cages are inaccessible to the adsorbate molecules.²⁶

of ΔH_{ads} over the central portion of the curve indicates that the majority of the adsorption sites (Brønsted sites) are homogeneous in nature with respect to benzene adsorption and that no sorbate–sorbate interactions occur under the prevailing conditions. This may be interpreted to mean that the *acidic sites* within the sample are homogeneous in *strength*, with the possible exception of a few stronger sites. Barrer et al.¹⁵ reported a slight decrease in the molar differential heats of adsorption from 75 to 71 kJ mol⁻¹ with increasing coverage for dehydrated zeolite X, Si/Al = 1.33 (determined through analysis of adsorption isotherms). Their higher values of ΔH_{ads} are probably due to the presence of a larger number of Na⁺ cations in their zeolite X sample compared to the H-Y sample studied here. Likewise, their somewhat higher saturation coverage (43 benzene molecules/u.c. at 323 K) is probably due to the higher aluminum content of their zeolite X framework, which increases the number of adsorption sites, favoring benzene adsorption. A decrease in ΔH_{ads} with adsorbate coverage is commonly due to the often inhomogeneous nature of adsorption sites within the zeolite. Adsorbate molecules preferentially adsorb onto the strongest sites, and thus the heats generated gradually decrease as the adsorption sites are “titrated” in order of decreasing strength. Thamm and Regent¹⁶ described an *increasing* ΔH_{ads} with coverage (from 77.9 to 87.1 kJ mol⁻¹) when adsorbing benzene onto zeolite Na–Y (Si/Al = 2.37) at 301 K. They attribute the high heats of adsorption to interaction between benzene and Na⁺ cations, such that the sodium sits on the 6-fold symmetry axis of the benzene

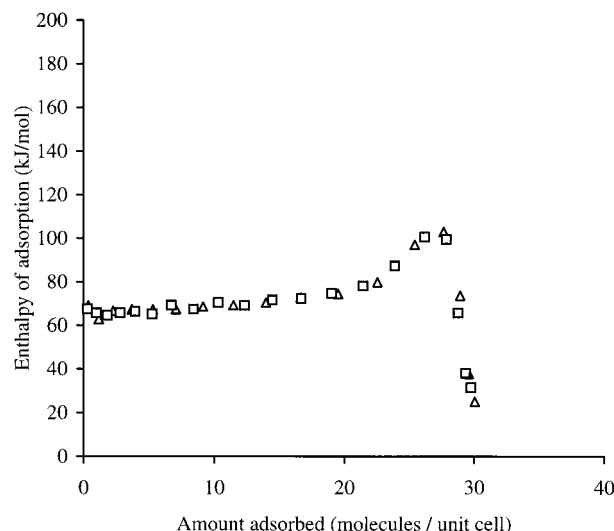


Figure 2. Enthalpy of adsorption of ethylbenzene onto H-Y versus sorbate coverage at 323 K. Two sets of data were measured under identical conditions.

molecule. No explanation is given for the increase in ΔH_{ads} with coverage. Similar results have been reported for the adsorption of benzene onto zeolite Na-X.¹⁷ Unusual behavior was found for the adsorption of benzene onto silicalite (theoretical Si/Al = ∞) at 301 K.^{18,19} Several minima in the curve of ΔH_{ads} versus coverage, with a general trend toward higher heats were observed. The authors attributed this to the mutual interaction between benzene molecules, forming, in one stage, dimers, and, in another, larger clusters, etc. In the case of the present work, the formation of oligomers is assumed to be absent, since ΔH_{ads} was invariant with coverage over the majority of sorbate loadings. Recently, Szabelski et al.²⁰ have re-interpreted the results of Thamm¹⁸ on the basis of a statistical model. With this model, good agreement between experiment and theory was obtained for sorption of benzene and *p*-xylene in silicalite assuming cooperative redistribution of molecules adsorbed on three types of sites coinciding with the inflection points on the isotherms.

Figure 2 shows two sets of data measured under identical conditions for the adsorption of ethylbenzene onto two separately prepared H-Y samples. The differential heats of adsorption were found to increase with coverage from approximately 65 to 105 kJ mol⁻¹ over the range 2–28 molecules/u.c. as Brønsted sites are titrated. The ΔH_{ads} increases slightly from 65 \pm 5 to 80 \pm 5 kJ mol⁻¹ over the range 2 to 22 molecules/u.c. The increase is more abrupt from 80 \pm 5 to 105 \pm 5 kJ mol⁻¹ over the range 22–28 molecules/u.c. The increase of ΔH_{ads} with coverage may be associated with mutual sorbate–sorbate interaction, which contributes to the exothermicity of the adsorption. This phenomenon has been observed before for various systems including benzene, *p*-xylene,¹⁸ and various *n*-alkanes¹⁹ on silicalite and various *n*-alkanes²¹

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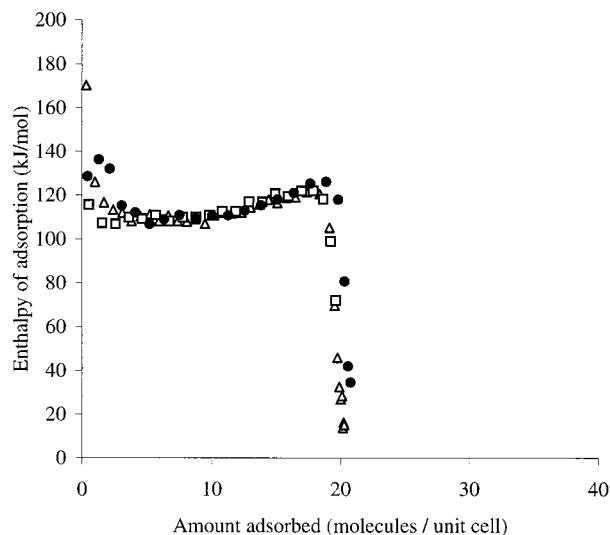


Figure 3. Enthalpy of adsorption of 1,3- and 1,4-diethylbenzene onto H-Y versus sorbate coverage at 323 K. Two sets of data for 1,4-diethylbenzene (open symbols) and 1,3-diethylbenzene (filled symbols) were all measured under identical conditions.

and benzene on Na faujasites.^{16,17} In the case of alkanes, large differences in the heats of adsorption of the same sorbate onto faujasites of differing Si/Al ratios were attributed to differences in the polarization interaction between the sorbate and the zeolite. The reason for the two-stage increase in ΔH_{ads} with coverage seen in the present work is unclear but could be attributed to the contribution of a second type of sorbate-sorbate interaction once approximately 22 molecules have been adsorbed per u.c. A sharp cutoff in the differential enthalpy of adsorption is observed in Figure 2 at 28 molecules/u.c., and physisorption of the sorbate becomes dominant above loadings of 30 ethylbenzene molecules/u.c. The slope of the cutoff is much steeper than in the case of benzene, and the number of ethylbenzene molecules which can be accommodated in the pore volume of H-Y is less than that of benzene on account of the higher molecular volume of ethylbenzene (Table 2). Interestingly, the differential enthalpies of adsorption of benzene and ethylbenzene observed at moderate coverages (10–20 molecules/u.c.) are similar to those determined from isosteres of benzene and ethylbenzene adsorbed onto zeolite H-ZSM-5 (i.e., 64 ± 5 and 82 ± 5 kJ mol⁻¹, respectively).^{22,23}

The curves of ΔH_{ads} versus coverage for 1,3- and 1,4-diethylbenzene adsorbed onto H-Y are similar to one another and are shown in Figure 3. The average differential enthalpies of adsorption are much higher than those which were seen for benzene and ethylbenzene. This increase in differential adsorption enthalpy may be attributed to the greater electron density in the aromatic rings of the ethyl-substituted sorbates, due to the electron-donating properties of alkyl groups. The increased electron density gives a stronger interaction with positively charged centers in the zeolite. Relatively higher differential heats were seen in the initial portions of the curves, followed by a drop and then by a gradual increase in ΔH_{ads} from approximately 110 ± 5 to 125 ± 6 kJ mol⁻¹ with coverage. During this latter period, the adsorbates interact with Brønsted sites. The cutoff which occurs once the pore

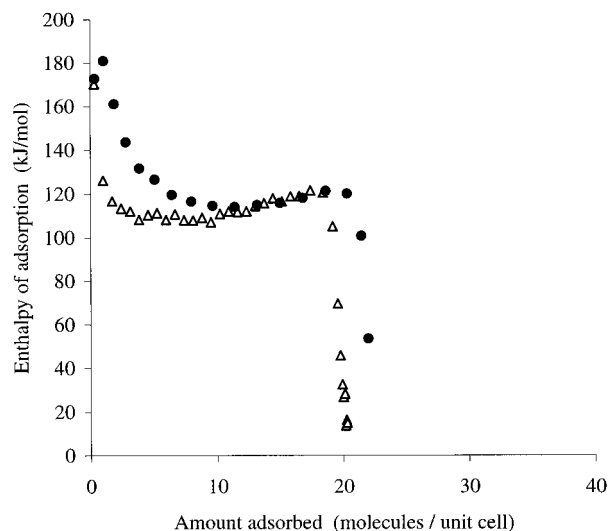


Figure 4. Enthalpy of adsorption of 1,4-diethylbenzene onto Na_{0.7}H-Y (0.7 Na⁺/u.c.; filled symbols) versus sorbate coverage at 323 K. Data for adsorption of 1,4-diethylbenzene onto H-Y (0.25 Na⁺/u.c.; open symbols) are included for comparison.

volume is saturated with sorbate is even more sudden than in the case of ethylbenzene and occurs at a lower loading of 20 molecules/u.c., in accordance with the larger molecular volume of the diethylbenzenes (Table 2).

All of the above results (Figures 1–3 and Table 1) showed that a small number of adsorption sites exist in the zeolite Y sample, which are relatively much stronger than the majority of sites. This was manifested in the liberation of relatively large amounts of heat on adsorption of the first few molecules per unit cell of any of the adsorbates.

Interaction of adsorbate molecules with extraframework Na⁺ ions may be responsible, in part, for the high initial values of ΔH_{ads} seen in Figures 1–3. To demonstrate the affect of the alkali cations, adsorption of 1,4-diethylbenzene onto a sample containing 0.7 Na⁺/u.c., Na_{0.7}H-Y, was measured. Figure 4 shows the results, in comparison with those for H-Y (which contains only 0.25 residual Na⁺/u.c.). A marked increase in the number of strongly adsorbing sites upon introduction of an extra 0.45 Na⁺ ions/u.c. is seen clearly (data are summarized in Table 1). As has been seen for H-Y, increasing values of ΔH_{ads} with coverage were found after the initial high differential heats and subsequent drop. The numbers of adsorbate molecules/u.c. at which the enthalpies dropped to those of physisorption, marking saturation of the microporous volume, were similar for the two samples. The large ΔH_{ads} result from the strong interaction between the Na⁺ cations and the π -systems of the adsorbate molecules.

Interaction of sorbate molecules with Lewis acid sites often leads to relatively high adsorption heats compared to Brønsted sites.¹² Infrared spectroscopic analysis of sample H-Y following activation and subsequent sorption of pyridine allowed a quantitative measure of the ratio of Brønsted to Lewis acid sites to be obtained by comparing the absorbances of the various vibrational bands; see Figure 5. The vibrational band at 1543 cm⁻¹ was attributed to pyridine interacting with Brønsted sites, while that at 1453 cm⁻¹ was due to the interaction between pyridine and Lewis acid sites. Extinction coefficients from reference²⁴ were used to convert the absorbances into concen-

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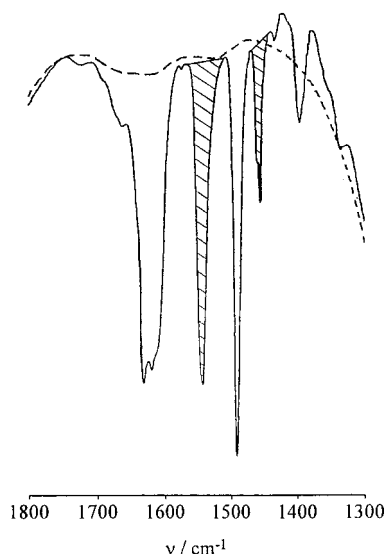


Figure 5. Infrared spectra of zeolite $\text{NH}_4\text{-Y}$ after activation at 673 K (H-Y, dashed curve) and subsequent adsorption of pyridine (continuous curve). Peaks at 1543 and 1453 cm^{-1} (shaded areas) are due to interaction of pyridine with Brønsted and Lewis acid sites, respectively.

trations, and peak areas were used in the calculations as opposed to peak heights. Such measurements revealed, in the case of the H-Y sample studied here, a Brønsted:Lewis acid site ratio of 3.6:1 (Figure 5). Results from X-ray powder diffraction and ^{27}Al MAS NMR showed that, before activation, the $\text{NH}_4\text{-Y}$ was highly crystalline and contained no detectable octahedral (extraframework) aluminum. After microcalorimetric measurements (i.e., activation, followed by adsorption of probe gas), XRD showed some of the crystallinity to have been lost (broader peaks and higher background), while ^{27}Al MAS NMR indicated 21–27% of the aluminum was in octahedral coordination. The presence of spinning sidebands from tetrahedral aluminum in some of the spectra may have rendered a slight inaccuracy in some of the calculated tetrahedral:octahedral Al intensity ratios since only the intensities of the central resonances were accounted for. Thus, the relative amount of extraframework aluminum may be less than that calculated. The NMR results are in relatively good agreement with those from IR spectroscopy with regard to the Brønsted:Lewis acid site ratios. If interaction of the adsorbates with Lewis acid sites were in part the reason for the initial high values of ΔH_{ads} which were seen in Figures 1–3, one would expect to see a higher proportion of these high differential heats.

To determine directly the effect of extraframework aluminum (true Lewis acid centers) on adsorbate interaction, a sample containing such sites, $\text{H-Y}_{\text{De-OH}}$, was measured. The results of adsorption of 1,4-diethylbenzene onto $\text{H-Y}_{\text{De-OH}}$ are shown in Figure 6. For comparison, one curve for the adsorption of 1,4-diethylbenzene onto the same sample prior to dehydroxylation ($\text{Na}_{0.7}\text{-Y}$) is also shown. The absence of large heats of interaction at low sorbate loading or, more specifically, the lack of any increase in the number of strongly adsorbed molecules over the parent material suggests that the extraframework aluminum sites are not the cause of the substantial differential heats seen in previous measurements (Figures 1–3), while residual Na^+ may be the cause (vide supra, Figure 4). The profile of the curve has an unusual shape which begins with a steep increase in ΔH_{ads} with loading, reaches a maximum, decreases, and then rises again gradually, approaching that value of ΔH_{ads} which was

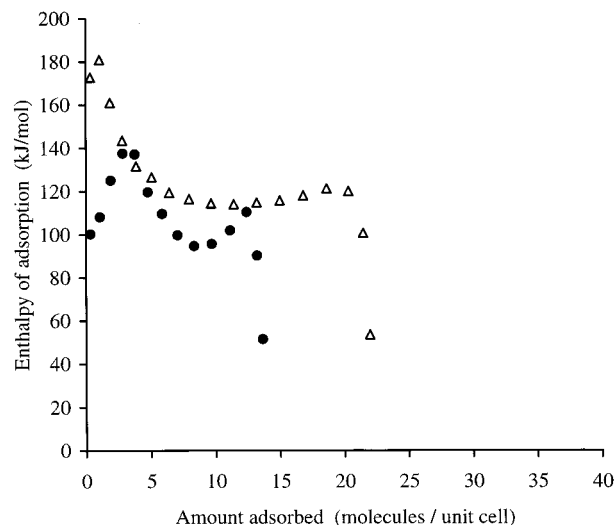


Figure 6. Enthalpy of adsorption of 1,4-diethylbenzene onto $\text{H-Y}_{\text{De-OH}}$ versus sorbate coverage at 323 K (filled symbols). Data for adsorption of 1,4-diethylbenzene onto the same sample prior to dehydroxylation are included for comparison (open symbols).

observed with H-Y. The latter effect is similar to the gradual increases seen earlier and is caused by sorbate–sorbate interaction; however, the initial sharp increase cannot be explained at this point in time. The cutoff in differential adsorption heat occurred at approximately 13 molecules/u.c., which is lower than in the nondehydroxylated sample. This effect is probably due to a partial loss of crystallinity, since the partially dehydroxylated sample was briefly exposed to air during preparation, which is detrimental.²⁵ The fact that the number of strongly adsorbed molecules has decreased on dehydroxylation, despite the sodium content remaining unchanged, points to a change in the physical nature and/or positioning of the Na^+ cations, which is to be expected during high-temperature treatment.

Conclusions

If one neglects initial high heats, differential enthalpies of adsorption for benzene and ethyl-substituted benzenes on H-Y zeolite were found to increase in the order benzene < ethylbenzene < 1,4-diethylbenzene \approx 1,3-diethylbenzene, with the majority of adsorption occurring on Brønsted acid sites.

Whereas a constant ΔH_{ads} was observed on adsorption of benzene over a wide range of coverages (ca. 2–27 molecules/u.c.), the substituted benzenes exhibited differential enthalpies which increased with sorbate loading. This phenomenon may be attributed to sorbate–sorbate interactions.

Once the zeolite pore volume became saturated, sharp cutoffs in ΔH_{ads} values were seen for all sorbates. In accordance with molecular volumes, the adsorbate coverage at which the inflection points were observed increased in the following order: 1,4-diethylbenzene \approx 1,3-diethylbenzene < ethylbenzene < benzene. The slope of the cutoffs became more steep as the size of the sorbate molecule increased.

On adsorption of the first few molecules per unit cell, relatively higher differential heats were evolved. In light of measurements performed on dehydroxylated and on

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partially Na-exchanged zeolite H-Y, the higher differential enthalpies could be ascribed to the presence of a small number of sodium cations in the zeolite, while extraframework aluminum (true Lewis acid sites) did not influence the adsorption strongly. Chemical analysis of the parent NH₄-Y sample revealed the presence of a small number of sodium atoms per unit cell, while infrared and ²⁷Al MAS NMR revealed that approximately 20% of the Al atoms in an activated sample possessed octahedral symmetry (i.e., extraframework, Lewis acid species).

The results obtained may explain why the disproportionation of ethylbenzene over zeolite catalysts has been

observed to be inhibited by the presence of diethylbenzenes (i.e., products of the reaction).^{9,10}

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