

Temperature-Programmed Desorption and Infrared Spectroscopic Studies of Benzene Adsorption in Zeolite ZSM-5

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The adsorption and desorption of benzene over the zeolite H-ZSM-5 has been investigated using simultaneous Fourier transform infrared (FTIR)–temperature-programmed desorption (TPD) measurements. The adsorption was studied as a function of benzene loading and the Si/Al ratio of the zeolite. FTIR and TPD confirm the existence of two types of sites for the adsorption of benzene in H-ZSM-5: Brønsted and non-Brønsted sites, with the latter located at the center of the intersection voids. The Brønsted sites are the favored sites for adsorption, and adsorption on the non-Brønsted sites occurs only after these sites are filled. There is no evidence for clustering or interaction between benzene molecules adsorbed on either the Brønsted or non-Brønsted sites.

Introduction

Understanding the nature of the interaction of aromatic molecules with the surface of zeolites is important for a better appreciation of how zeolites behave as catalysts for alkylation and cracking reactions. The synthetic zeolite ZSM-5 and its purely siliceous analogue are one of the most widely studied zeolites. It is one of the most versatile and commercially significant zeolites; it is widely used in the petroleum industry to convert methanol to more-complex hydrocarbons—the methanol-to-gasoline (MTG) process—as well as in the alkylation of aromatics and their subsequent separation.^{1–4} ZSM-5 is a medium-pore zeolite, the structure of which consists of a set of sinusoidal channels intersecting a set of straight channels, each with 10-membered rings.⁵ The diameter of the circular sinusoidal channels is 5.4 Å and that of the elliptical straight channel is 5.7–5.1 Å, whereas the intersections, which are almost spherical, have a diameter of 8.7 Å. The channels are just large enough to accommodate a benzene molecule, and, consequently, the diffusion and adsorption of alkylated aromatics are rapidly attenuated as bulkier substituents are attached to the benzene ring. It is this property of ZSM-5, the “shape selectivity”, that makes it such an important catalyst. In addition, the isomorphous substitution of Si by Al allows for the introduction of Brønsted acid sites and, because the Si/Al ratio can be varied, the concentration of acid sites also can be varied. The behavior of an adsorbate molecule trapped within ZSM-5 is dictated both by the porous architecture of the zeolite and specific interactions with the Brønsted or acid sites. Because the application of ZSM-5 is, in many cases, related to the interaction of the adsorbate with the zeolite, it is important to establish the relative importance of these two factors. In the present study, we have examined the adsorption of benzene in H-ZSM-5 zeolites with varying Si/Al ratios using temperature-programmed desorption (TPD) measurements, while simultaneously monitoring the adsorbed species using Fourier transform infrared (FTIR) spectroscopy. The objective was to delineate and evaluate the

relative importance of Brønsted and non-Brønsted sites for the adsorption of benzene in H-ZSM-5.

The adsorption of benzene in ZSM-5 has been extensively studied by a variety of techniques, both experimental and theoretical, as would be expected for a problem of such importance. Adsorption isotherm measurements⁶ have shown that, in H-ZSM-5, the incorporation of the Al atom leads to the creation of additional sites for the adsorption of benzene. It was also concluded from the observation that the differential molar enthalpy of sorption was a constant for loading levels up to 6 benzene molecules per unit cell (uc) (the maximum loading in Silicalite-1 is 8.5 benzene molecules) that the benzene molecules within the zeolite do not interact with each other. Subsequent calorimetric studies⁷ confirmed these results; the heat of sorption was observed to be a constant up to ~4 benzenes/uc. At higher loading levels, changes in the heat of sorption with loading was observed. This was attributed to adsorption on energetically less favorable sites, as well as cooperative interaction between the adsorbed benzene molecules. However, these changes in enthalpy could also result, as shown by subsequent X-ray diffraction (XRD)⁸ and Raman spectroscopic studies,⁹ from structural changes in the zeolite at higher loading. At loading levels above 4 benzene molecules/uc of Silicalite-1, the structure transforms from monoclinic to orthorhombic.

The location of the benzene molecules in Silicalite-1 has been explored by both theoretical calculations and diffraction experiments.^{10–14} Theoretical studies predict that benzene is favorably located at three positions in Silicalite-1: in the intersections, in the straight channels, and in the sinusoidal channels. A recent neutron diffraction study found that, at a loading level of 3.4 benzene molecules/uc of Silicalite-1, the best agreement with the experiment was obtained when benzene molecules are located in mutually exclusive positions in the intersection of the straight and sinusoidal channels. At higher loading (7.5 mol/uc), all three sites—the intersection and the straight and sinusoidal channels—are occupied. The intersections of the straight and sinusoidal channels are the most-favored locations. Its dimensions (diameter of 8.7 Å) allow the adsorbed benzene molecules much greater orientational mobility, as compared to either the straight or sinusoidal channels.¹⁵

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Infrared (IR) spectroscopic studies of the adsorption of benzene on H-ZSM-5 and alkali-metal ion-exchanged ZSM-5 have been reported recently.^{16,17} The C–H stretching and the combination C–C stretching vibration modes of benzene that appear between 3200 and 3000 cm^{-1} showed no change in position either with loading or with changes of the extra framework cation. The in-plane C–C stretching band of benzene that appears at 1479 cm^{-1} also showed no change. However, the C–H out-of-plane bending modes, which appear at 1815 and 1960 cm^{-1} in liquid benzene, were split on adsorption in H-ZSM-5, even at loading levels as low as 1.6 mol/uc. Based on the fact that the C–H out-of-plane modes of benzene split into doublets when liquid benzene transforms to solid benzene (the in-plane fundamental modes show no change during this transformation), the authors concluded that the adsorbed benzene also must be “compressed”, even at loading levels as low as 1.6 mol/uc. Therefore, the IR results were interpreted in terms of the formation of benzene clusters. The clustering was envisaged to occur as a result of the packing of benzene molecules side by side with their planes parallel to the walls of the zeolitic channel. The π – π interactions were considered to be responsible for the splitting of the out-of-plane vibrational modes.

The results of the IR spectroscopic measurements^{16,17} are in apparent contradiction with the calorimetric experiments⁷ and, to some extent, the diffraction experiments,^{8,13} in regard to the loading levels of benzene in ZSM-5 at which benzene–benzene sorbate interactions or clustering is important. Although calorimetric and adsorption studies indicate that “clustering”, if it does exist, is significant only above a loading of 4 mol/uc in Silicalite-1, the IR results of benzene in H-ZSM-5 have been interpreted in terms of cluster formation at a much lower loading level (1.6 mol/uc). One of the objectives of the present FTIR–TPD study was to evaluate the importance of clustering when benzene adsorbs on the zeolite H-ZSM-5.

Experimental Section

IR spectra were recorded on a Perkin–Elmer model Spectrum-2000 FTIR spectrometer in the diffuse reflectance mode, using a DRIFT (P/N 19900 series) accessory with a liquid- N_2 -cooled MCT detector. The sample chamber consisted of a water-cooled stainless-steel block with a zinc selenide (ZnSe) window. Sample temperatures could be controlled in the range of 273–773 K and could also be ramped at rates of 10–20 K/min for TPD measurements. The sample chamber was connected to a gas-handling manifold and also on-line to a quadrupole mass spectrometer (an SRS model QMS300 series gas analyzer). The zeolite samples were activated in the IR sample chamber by heating in a stream of helium at 673 K for 2 h, prior to dosing with known volumes of benzene. IR spectra were collected by co-adding 128 scans at a resolution of 4 cm^{-1} . The zeolite, which was activated under similar conditions as those in the adsorption measurements, was used to record the background spectra. Therefore, the IR spectra reported here are difference absorbance spectra of the zeolite with and without adsorbed benzene. For the variable-temperature measurements, the background spectra also were recorded at different temperatures. The TPD measurements and the IR spectra were recorded with helium carrier gas flow rates maintained at 30 cm^3/min .

H-ZSM-5 zeolite was prepared by exchanging the Na^+ ions in Na-ZSM-5 (Si/Al = 16.4, 20, and 125) with ammonium (NH_4^+) ions, followed by calcination at 823 K in flowing air for 5 h. The siliceous polymorph of ZSM-5, Silicalite-1, was synthesized, using sodium silicate as the source of SiO_2 and

tetrapropylammonium bromide (TPABr) as the template, following the procedure given in the work by Robson.¹⁸ Silicalite-1 was crystallized from a gel of composition $\text{SiO}_2\text{:TPABr:NH}_4\text{F:H}_2\text{O}$ in the ratio 1:0.08:0.04:20 by heating at 393 K for 120 h in a Teflon-lined autoclave under autogenous pressure. The Silicalite-1 sample was calcined at 773 K in flowing oxygen to remove all traces of the organic template from the lattice. The crystallinity of the zeolites was checked by recording the powder XRD patterns (using a Shimadzu model XD-D1 powder X-ray diffractometer with Cu $\text{K}\alpha$ radiation) and was determined to be comparable (see Supporting Information).

Results and Discussions

Temperature-Programmed Desorption. The TPD profiles of benzene, as a function of loading over H-ZSM-5 zeolites with differing Si/Al ratios (including the purely siliceous Silicalite-1), are shown in Figure 1a–d. The simplest is the TPD from Silicalite-1; the desorption shows a single maximum, with the intensity increasing as the loading increases, but no significant change in the temperature of the desorption maxima.

The TPD of benzene from H-ZSM-5 shows systematic changes as a function of loading, as well as the Si/Al ratio of the zeolite. At low loading, the desorption shows a broad maxima between 565 K and 500 K. With increasing loading, an additional maximum develops at lower temperatures. The temperature of this maximum (400 K) coincides with that of the single peak in the TPD of benzene over Silicalite-1 (see Figure 1a). The low-temperature maximum grows in intensity with loading, but its position remains unchanged. At maximum loading, it is the low-temperature maxima at 400 K that is the dominant feature of the TPD profile. The temperatures of the desorption maxima are independent of the Si/Al ratio; however, the relative contribution of the high-temperature peak to the overall desorption profile decreases as the Si/Al ratio increases. In Silicalite-1, this feature is completely absent. Therefore, it is reasonable to conclude that the high-temperature maxima are due to benzene molecules that are associated with the Brønsted sites of ZSM-5. Interestingly, note that, in situations where the high-temperature maxima are present in the TPD, it is this site that becomes occupied prior to adsorption on the site for which the desorption maxima occurs at 400 K. It may be seen that, at loading levels above which the low-temperature (400 K) peak appears, the increase in the intensity of the high-temperature desorption maxima is considerably less than that of the low-temperature peak. For the H-ZSM-5 zeolite with Si/Al = 16.4, there is, in fact, no further increase in the intensity with loading after the low-temperature desorption appears.

To summarize, the TPD results indicate that there are two types of adsorption sites available for the benzene molecules in ZSM-5. Of these, one is present only in the acid form and is the energetically more favored of the two sites and, consequently, is occupied first. The relative contribution of the two features varies with the loading; however, their positions are unaffected, which suggests that, for the loading levels studied, the interaction between adsorbed benzene molecules is not significant.

Infrared Spectra. The state of the adsorbed benzene during the TPD measurements was simultaneously monitored via FTIR spectroscopy. The room-temperature spectrum of benzene adsorbed on Silicalite-1 and H-ZSM-5 (Si/Al = 16.4) at maximum loading is shown in Figure 2. The positions of the bands and their relative intensities showed no change with loading. The positions of the bands and their assignments are given in Table 1. The spectral features have been assigned based

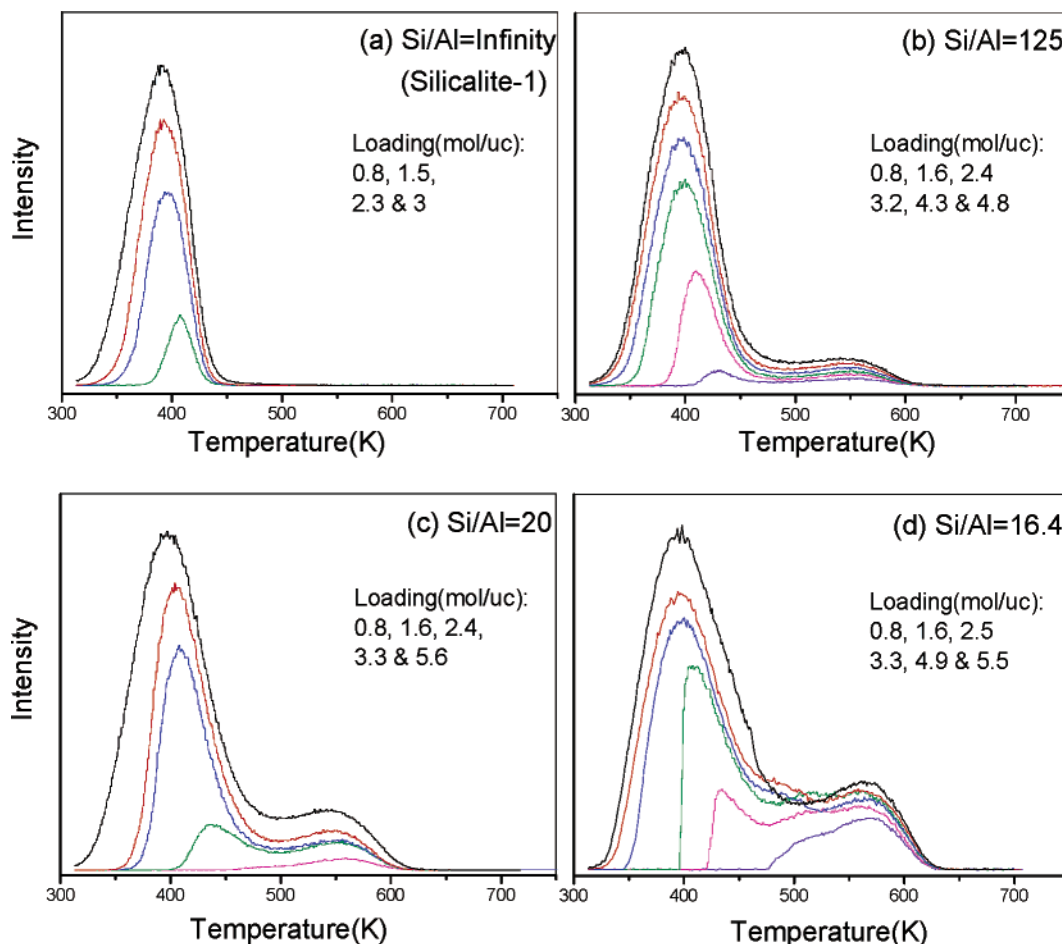


Figure 1. Temperature-programmed desorption (TPD) of benzene, at different loading levels, over zeolite H-ZSM5 with differing Si/Al ratios. The ratios, as well as the loading levels, are indicated in each panel.

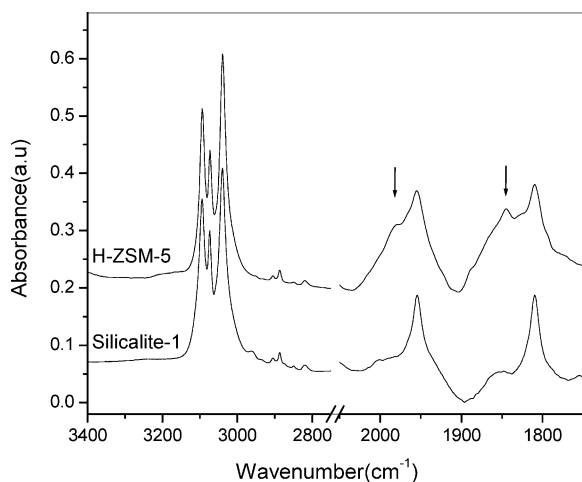


Figure 2. Infrared (IR) spectra of benzene adsorbed on Silicalite-1 and H-ZSM-5 in the C–C/C–H stretching mode and C–H out-of-plane bending mode regions.

on the corresponding features that appear in the gas-phase spectrum of benzene.¹⁹ As mentioned in the Experimental Section, the spectra were recorded as difference absorption spectra; consequently, there is no contribution from the framework vibrations of the zeolite in the spectra shown in Figure 2. Attention is focused on the C–C and C–H stretching modes that appear between 3000 cm^{-1} and 3100 cm^{-1} and the C–H out-of-plane bending modes, which appear between 1800 cm^{-1} and 2000 cm^{-1} . In the gas phase, the C–C stretching ($\nu_{19} + \nu_8$) mode, the C–C stretching plus bending ($\nu_1 + \nu_6 + \nu_{19}$)

mode, and the C–H stretching (ν_{20}) mode appear at 3047, 3073, and 3099 cm^{-1} , respectively. For benzene adsorbed on Silicalite-1 and H-ZSM-5, these features appear at 3039, 3072, and 3093 cm^{-1} in the room-temperature spectrum (Figure 2). There is no significant change in the positions of the stretching modes of the adsorbed benzene from the corresponding gas-phase values. In the C–H bending or ring breathing mode region, the spectra of benzene on Silicalite-1 shows bands at 1810 and 1954 cm^{-1} , corresponding to the C–H out-of-plane bending vibrations ($\nu_{10} + \nu_{17}$) and ($\nu_5 + \nu_{17}$), respectively. These values are identical to the corresponding gas-phase values. For benzene adsorbed on H-ZSM-5, it may be seen that both features at 1810 and 1954 cm^{-1} have a pronounced shoulder at higher frequencies (1844 and 1980 cm^{-1} , respectively, as indicated by arrows in Figure 2). These features are also observed in the spectra of benzene adsorbed on the H-ZSM-5 zeolites with Si/Al ratios of 20 and 125 (however, those for the latter are not as pronounced). Therefore, the peaks at 1844 and 1980 cm^{-1} may be assigned to the out-of-plane bending vibrations of benzene molecules adsorbed on Brønsted sites of H-ZSM-5.

The assignment of the features at 1844 and 1980 cm^{-1} in the spectrum of benzene on H-ZSM-5 to benzene molecules adsorbed on Brønsted sites is in agreement with the assignments of Su et al. of benzene adsorbed on Na- β and EMT zeolites.^{20–22} These authors had, in addition to the bands at 1844 and 1982 cm^{-1} , observed bands at 1868 and 2000 cm^{-1} that were assigned to benzene molecules located at the 12 ring O windows of the zeolite. These are not observed in the present spectra. In a recent IR study^{16,17} of benzene on alkali-metal and proton-exchanged

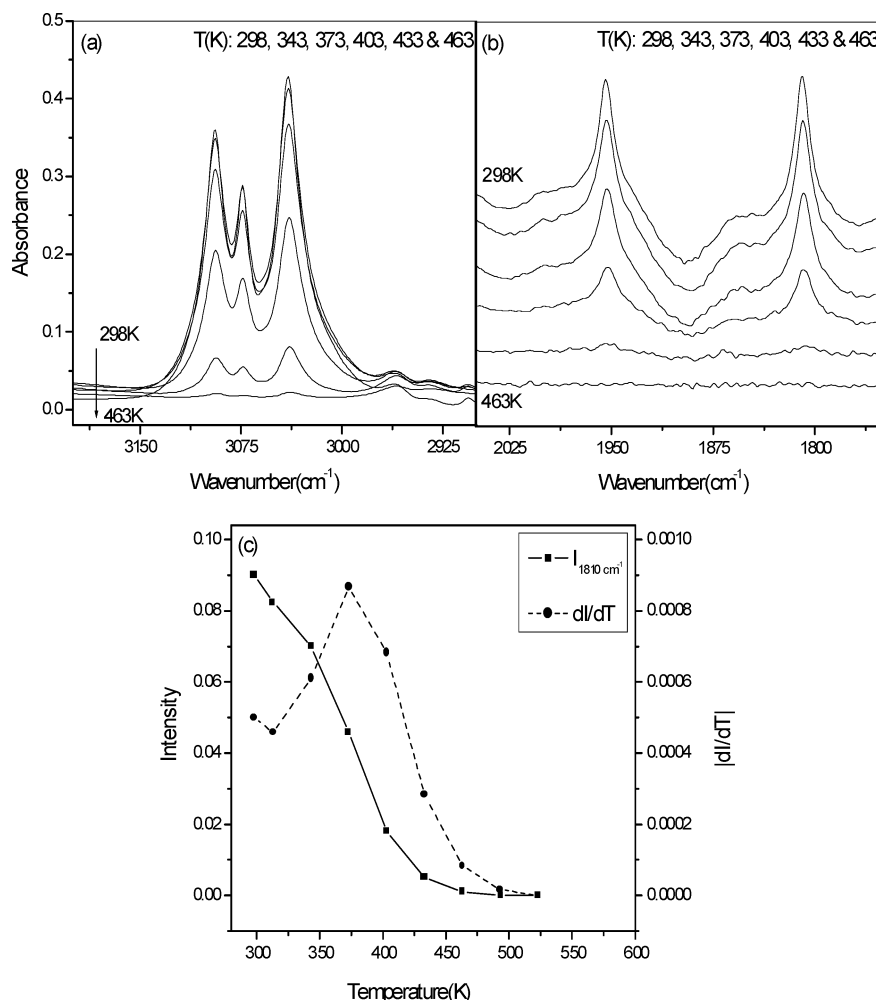


Figure 3. Variable-temperature IR spectra of benzene on Silicalite-1: (a) the C–H and C–C stretching region, (b) C–H out-of-plane bending region, and (c) temperature variation of the intensity of the C–H out-of-plane bending mode at 1810 cm^{-1} ; the dashed line represents the derivative plot.

TABLE 1: Vibrational Assignments for Benzene Adsorbed on Silicalite-1 and H-ZSM-5

gas-phase benzene (cm^{-1})	benzene adsorbed on Silicalite-1 (cm^{-1})	benzene adsorbed on H-ZSM-5 (cm^{-1})	assignment
3099	3093	3093	ν_{20} (C–H stretching)
3073	3072	3072	ν_1 (C–C stretching) + ν_6 (C–C stretching) + ν_{19} (C–C–C bending)
3047	3039	3039	ν_{19} (C–C stretching) + ν_8 (C–C stretching)
1956	1954	1954	ν_5 (C–H bending \perp) + ν_{17} (C–H bending \perp)
		1980	ν_5 + ν_{17} (benzene on Brønsted acids)
1810	1810	1810	ν_{10} (C–H bending \perp) + ν_{17} (C–H bending \perp)
		1844	ν_{10} + ν_{17} (benzene on Brønsted acids)
1482	1478	1478	ν_{19} (C–C stretching)

ZSM-5, a splitting of the out-of-plane bending modes into two pairs of doublets was interpreted as being characteristic of the clustering of adsorbed benzene molecules involving π – π interactions. The splitting of the benzene out-of-plane bending modes on adsorption was considered to be analogous to the splitting of the 1815 and 1960 cm^{-1} into two sets of bands, at 1825 and 1836 cm^{-1} and at 1972 and 1980 cm^{-1} , when benzene transforms from the liquid to the solid. The present assignment of the features at 1844 and 1980 cm^{-1} as being due to benzene adsorbed on Brønsted sites is based on a comparison of the spectra of benzene on H-ZSM-5 and the isostructural Silicalite-1, where such sites are absent and these peaks are not observed, is straightforward and unambiguous. In addition, the band positions show no change with loading, which also excludes any significant interaction between adsorbed benzene molecules. To summarize, the IR studies indicate that there are two types

of benzene in H-ZSM-5: an almost gas-phase-like benzene (the vibrational frequencies are similar to that of benzene in the gas phase) and benzene adsorbed on Brønsted sites. Only the first is present in Silicalite-1.

Variable-Temperature Infrared Spectra. The IR spectrum of the adsorbed benzene was monitored during the TPD measurement. The variable-temperature spectra of benzene adsorbed on Silicalite-1 and H-ZSM-5 were recorded in the temperature range of 298 – 673 K . The variable-temperature spectrum of benzene on Silicalite-1 in the stretching mode region (3000 – 3100 cm^{-1}) and bending mode region (1800 – 2000 cm^{-1}) are shown in Figure 3a and 3b, respectively (the loading corresponds to a maximum of $\sim 3\text{ mol/uc}$). In both regions of the spectra, the positions of the bands show no change with temperature. The intensities show a steady decrease with temperature and are completely absent by 450 K . This is a

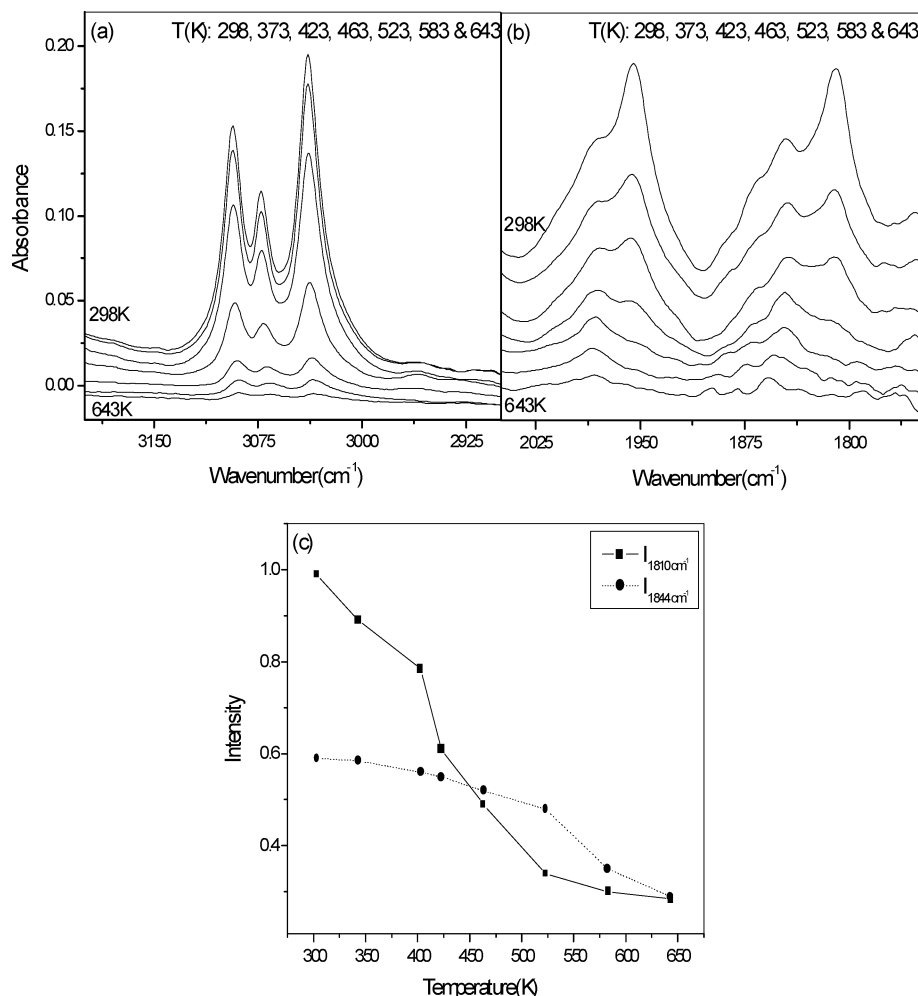


Figure 4. Variable-temperature IR of benzene on H-ZSM-5 showing (a) the C–H and C–C stretching region, (b) the C–H out-of-plane bending region, and (c) the temperature variation of the intensity of the C–H out-of-plane bending modes at 1810 and 1844 cm^{-1} for benzene adsorbed over H-ZSM-5.

straightforward reflection of the fact that the concentration of adsorbed benzene decreases as the temperature increases, because of desorption. The integrated intensity (I) of the C–H out-of-plane bending ($\nu_{10} + \nu_{17}$) mode at 1810 cm^{-1} , as a function of temperature, is plotted in Figure 3c, along with the differential, $|dI/dT|$. The temperature at which the intensity of the 1810 cm^{-1} peak shows a decrease (405 K) agrees reasonably with the temperature at which the rate of desorption is a maximum in the TPD profile. The intensity variations of the stretching modes, as well as the out-of-plane ($\nu_5 + \nu_{17}$) bending mode at 1954 cm^{-1} , are similar.

The variable-temperature IR spectrum of benzene on H-ZSM-5 in the C–H/C–C stretching mode (3000–3100 cm^{-1}) and the out-of-plane bending mode (1800–2000 cm^{-1}) regions are shown in Figure 4a and 4b, respectively. The loading corresponds to 5.5 mol/uc. The stretching modes show no change in position or relative intensity with temperature. There is a decrease in the overall intensity of the spectra with temperature, which reflects the decreased concentration of adsorbed benzene due to desorption.

The temperature variation of the intensity of the out-of-plane ring breathing modes ($\nu_{10} + \nu_{17}$) and ($\nu_5 + \nu_{17}$) are shown in Figure 4b. It may be seen that the intensity of the 1810 and 1954 cm^{-1} peaks that had been assigned to an almost “gas phase-like benzene” decreases rapidly with temperature, as compared to that of the 1844 and 1980 cm^{-1} peaks that had been assigned to benzene adsorbed on Brønsted sites. This may

be seen more clearly in Figure 4c, where the intensity of the 1810 and 1844 cm^{-1} bands have been plotted as a function of temperature. The intensity of the 1810 cm^{-1} band shows a decrease at 400 K, whereas for the 1844 cm^{-1} band, the decrease occurs at 500 K. The intensity variations of the bands at 1954 and 1980 cm^{-1} are similar.

From a comparison of the temperature variation of the IR intensities (Figure 4c) with the TPD profiles of benzene over H-ZSM-5 (see Figure 1), it is possible to identify the species associated with each of the maxima in the TPD profile. The desorption maxima that appear at lower temperatures in the TPD is due to a “gas-phase-like benzene” and the high-temperature desorption is due to benzene adsorbed on a Brønsted site. This conclusion is similar to that which was concluded from a comparison of the TPD profiles for benzene desorption over ZSM-5 zeolites of varying Si/Al ratios (see Figure 1). The positions of the IR bands of benzene on H-ZSM-5 and Silicalite-1 showed no change with decreases in the concentration of adsorbed benzene as the temperature is increased, indicating the absence of any direct benzene–benzene interaction; this conclusion is similar to that determined from TPD measurements.

Conclusions

The adsorption and desorption of benzene over the MFI zeolite H-ZSM-5 has been investigated using a simultaneous

Fourier transform infrared (FTIR)—temperature-programmed desorption (TPD) measurement. The adsorption was studied as a function of benzene loading and the Si/Al ratio of the zeolite. The TPD of benzene over ZSM-5 showed two main features, with the lower-temperature feature appearing only at high loadings. The positions of the two maxima do not change with loading. The two features are assigned to desorption from Brønsted and non-Brønsted sites, respectively, based on the fact that desorption from the aluminum-free Silicalite-1 gave a single maximum whose temperature was identical to that of the lower-temperature maximum in the TPD of benzene over H-ZSM-5.

The existence of two types of sites was also confirmed by FTIR measurements, which were recorded during the TPD run. From a comparison of the spectral features of benzene adsorbed on H-ZSM-5 and Silicalite-1, it was possible to unambiguously identify vibrational features of benzene adsorbed on the Brønsted sites. For benzene adsorbed on the non-Brønsted sites, the vibrational features are similar to that of benzene in the gas phase. These benzene molecules, according to molecular modeling calculations¹² of benzene in Silicalite-1 and diffraction experiments,¹³ are likely to be molecules located in the center of the intersections of the straight and sinusoidal channels. The dimension of the intersection voids allows the molecule to rotate freely. The Brønsted sites are the favored sites for adsorption, and only after these sites are filled does adsorption on the non-Brønsted sites occur. The IR peak positions do not change with loading or temperature, indicating that clustering or interaction between benzene molecules adsorbed on either the Brønsted sites or non-Brønsted sites is not significant, either in Silicalite-1 or H-ZSM-5, for the loadings studied.

Supporting Information Available: X-ray diffractograms of calcined H-ZSM-5 (Si/Al = 16.4, 20, and 125) and

Silicalite-1 (PDF). This material is available free of charge via the Internet at <http://pubs.acs.org>.

References and Notes

- (1) Bhatia, S. *Zeolite Catalysis: Principles and Applications*; CRC Press: Boca Raton, FL, 1990.
- (2) Chang, C. D. *Catal. Rev. Sci. Eng.* **1983**, 25, 1.
- (3) Chen, N. Y.; Garwood, W. E.; Heck, R. H. *Ind. Eng. Chem. Proc. Des. Dev.* **1987**, 26, 207.
- (4) Stocker, M. *Microporous Mesoporous Mater.* **1999**, 29, 3.
- (5) Meier, W. M.; Olson, D. H. *Atlas of Zeolite Structure Types*; Butterworth—Heinemann: London, 1992.
- (6) Pope, C. G. *J. Phys. Chem.* **1986**, 90, 835.
- (7) Thamm, H. *J. Phys. Chem.* **1987**, 91, 8.
- (8) Mentzen, B. F.; Lefebvre, F. *Mater. Res. Bull.* **1997**, 32, 813.
- (9) Huang, Y.; Havenga, E. A. *J. Phys. Chem. B* **2000**, 104, 5084.
- (10) Ramdas, S.; Thomas, J. M.; Betteridge, P. W.; Cheetham, A. K.; Davies, E. K. *Angew. Chem. Int. Ed. Engl.* **1984**, 23, 671.
- (11) Maeder, F. V.; Jobic, H. *Chem. Phys. Lett.* **1990**, 169, 31.
- (12) Forester, T. R.; Smith, W. J. *Chem. Soc. Faraday Trans.* **1997**, 93, 3249.
- (13) Goyal, R.; Fitch, A. N.; Jobic, H. *J. Phys. Chem. B* **2000**, 104, 2878.
- (14) Sacerdote, M.; Bosselet, F.; Mentzen, B. F. *Mater. Res. Bull.* **1990**, 25, 593.
- (15) Portsmouth, R. L.; Duer, M. J.; Gladden, L. F. *J. Chem. Soc. Faraday Trans.* **1995**, 91, 559.
- (16) Tripathi, A. K.; Sahasrabudhe, A.; Mitra, S.; Mukhopadhyay, S. R.; Gupta, N. M.; Kartha, V. B. *Phys. Chem. Chem. Phys.* **2001**, 3, 4449.
- (17) Sahasrabudhe, A.; Kamble, V. S.; Tripathi, A. K.; Gupta, N. M. *J. Phys. Chem. B* **2001**, 105, 4374.
- (18) Robson, H. *Microporous Mesoporous Mater.* **1998**, 22, 551.
- (19) Primet, M.; Garbowski, E.; Mathieu, M. V.; Imelik, B. *J. Chem. Soc. Faraday I* **1980**, 76, 1942.
- (20) Su, B.-L.; Manoli, J. M.; Potvin, C.; Barthomeuf, D. *J. Chem. Soc. Faraday Trans.* **1993**, 89, 857.
- (21) Su, B.-L. *J. Chem. Soc. Faraday Trans.* **1997**, 93, 1449.
- (22) Su, B.-L.; Norberg, V. *Langmuir* **1998**, 14, 7410.