On the Role of the Pore Size and Tortuosity for Sorption of Alkanes in Molecular Sieves

F. Eder and J. A. Lercher*

University of Twente, Department of Chemical Technology, 7500 AE Enschede, The Netherlands

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Adsorption of light alkanes on the acidic zeolites theta-1 (H-TON), ferrierite (H-FER), and ZK-5 (H-KFI) was studied by gravimetry, calorimetry, and infrared spectroscopy. Sorption of alkanes on the Brønsted acid sites is energetically favored, and the uptake at low alkane partial pressures is directly correlated to the concentration of acid sites. With H-FER, the accessibility of the two intersecting channel systems depends on the chain length of the alkanes. Although propane and *n*-butane sorb in both channels, the sorption of *n*-pentane is hindered in the 8-ring channels and sorption of *n*-hexane only occurs in the 10-ring channels. In the presence of cavities (such as found in H-KFI) pronounced intermolecular interactions between sorbed alkanes were monitored. In general, the heat of adsorption of alkanes increases with decreasing pore size. At pore sizes smaller than 0.5 nm repulsion forces start to be important, their impact being most prominent for larger isoalkanes.

Introduction

Traditionally, investigations focused on medium and large pore zeolites such as H-ZSM5 and H-FAU because of their utilization in large scale industrial processes such as fluid catalytic cracking.[1,2] In the last years, however, molecular sieves with a greater variety of pore sizes have attracted significant interest. Examples for this trend include large pore zeolites as catalysts for the alkylation of isoalkanes with alkenes[3,4] and zeolites with a smaller pore size than H-MFI, i.e, H-TON and H-FER as catalysts for the skeletal isomerization of olefins.[5−8] Although the catalytic effect of these materials is well established, the mechanistic aspects of these conversions are vividly debated.[6−8] In this context the sorption of hydrocarbons plays a critical role and our understanding of the microscopic and macroscopic aspects of the hydrocarbon−zeolite interactions might prove crucial for further catalyst development.

In general terms, sorption of hydrocarbons in zeolites has been frequently addressed and several models to describe the generic sorbate−sorbent interactions have been developed. In a conceptionally elegant approach Derouane et al.[9,10] related the strength of the interaction between alkane molecules and the zeolite lattice to the curvature of the pores. It was shown that the heat of adsorption of methane increases as the pore size decreases from FAU (0.74 nm) to MFI (∼0.55 nm). The heat of sorption was suggested to reach a maximum when the size of the adsorbed molecule and the size of the zeolite pores match. In agreement with these results McCullen et al.[11] showed that the heat of adsorption of *n*-butane on aluminophosphates decreases linearly as the pore size increases. A study by Stach et al.[12] addressing the sorption of *n*-alkanes and benzene on purely siliceous zeolites and on aluminophosphates with pores ranging from 0.55 nm (MFI) to 1.21 nm (VFI) shows a logarithmic dependence of the heat of adsorption on the framework density of the sorbent (which is inversely proportional to the pore size). It has to be emphasized, however, that the role of the tortuosity of the micropore channels, which is shown to be important by recent theoretical calculations[13] and experiments,[14] cannot be considered in this and most other global models.

Although these studies address the influence of the micropores surrounding the sorbed molecule, the role of the acid site (usually present in catalytically active materials) is not accounted for. Conceptually, the additional interaction between the acid site and the sorbed hydrocarbon can lead to synergistic and antagonistic effects depending on whether or not it redirects the alkanes to positions different from those preferred in the absence of acid sites.

The present report aims at a comparison of the sorption of alkanes in molecular sieves with pore openings smaller than 0.5 nm, i.e., TON, FER, KFI. The results are compared with data for sorption on other zeolites described earlier[15] in order to derive structure−property correlations for alkane sorption. IR spectroscopy, gravimetry, and calorimetry are the main means to characterize the interactions.

Experimental Section

Materials. H-FER and H-TON (Si/Al = 45) were provided by the Shell Research and Technology Center, Amsterdam. The H-TON samples with a Si/Al ratio of 52 and 64 were obtained from the Polish Academy of Science. H-KFI was supplied by Exxon Chemical Europe Inc. The chemical composition and concentration of the acid sites of the zeolite samples are compiled in Table 1. Propane, *n*-butane, and isobutane (purity is >99.5%) were obtained from Messer Griesheim Corp. and *n*-hexane, *n*-pentane, and isopentane (purity is >99.5%) from Fluka Chemie AG.

Gravimetry and Calorimetry. Measurements were performed with a modified SETARAM TG-DSC 111 instrument.[16] Approximately 15 mg of the NH_4 form of the samples was charged into the quartz sample holder of the balance and transferred into the hydrogen form by heating in vacuum ($p < 10^{-6}$ mbar) with a temperature increment of 10 K/min to 673K in the case of H-TON and H-FER and to 623 K in the case of H-KFI and holding that temperature for 1 h. After cooling to 333 K in the case of H-FER and H-TON and to 348 K in the case of H-KFI, the alkanes were discontinuously dosed into the closed system and equilibrated with the surface. The equilibration was confirmed by observing the heat flow and the changes in weight. If changes in pressure and weight and heat signal were not observed after admitting a dose, the system was considered to be equilibrated. The experiments were carried out in the pressure range 10^{-3}−13 mbar. Pressure was recorded with a BARATRON pressure transducer (Type 122A).

TABLE 1: Chemical Composition and Concentration of the Acid Sites of H-TON, H-FER, and H-KFI

|	Si/Al	H$^+$ conc [mmol/g][a]
H−FER	30	0.48
H-TON (1)	45	0.36
H-TON (2)	52	0.31
H-TON (3)	64	0.27
H-KFI	4	3.17

[a] Determined gravimetrically by ammonia adsorption at 373 K.
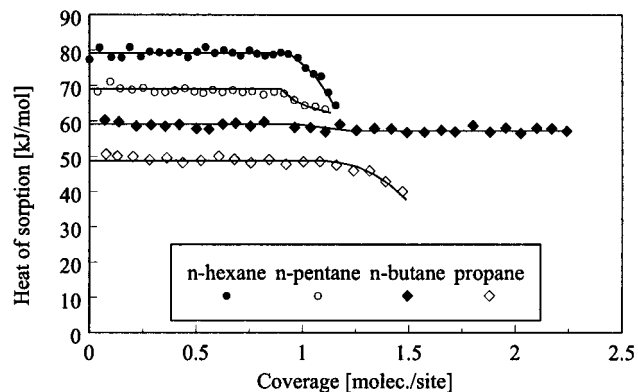
Figure 1. Differential heat of adsorption of *n*-alkanes on H-FER as a function of the coverage at 333 K.

The adsorption isotherms were determined gravimetrically simultaneously with the determinination of the differential sorption enthalpies. The isotherms on H-FER, H-TON, and H-KFI were fitted to a sum of Langmuir type adsorption isotherms considering the differences in the localized adsorption at the acid sites and delocalized sorption in the pores. The concentrations of acid sites used in the calculations were determined by ammonia adsorption/desorption (see Table 1).

Infrared Spectroscopy. Spectra were measured with a BRUKER IFS-88 spectrometer in the transmission absorption mode. The zeolites were pressed to self-supporting wafers and introduced into the heatable sample holder of a vacuum cell. The samples were activated by heating (673 K for FER and TON and 623 K for KFI) in vacuum ($p < 10^{-6}$ mbar) and holding this temperature for 1 h. The sorption experiments were carried out at 333 K in the case of H-FER and H-TON and at 348 K in the case of H-KFI and in a pressure range $10^{-3}-3$ mbar. The alkane partial pressure was increased stepwise, and after every step equilibration was followed by time resolved IR spectroscopy. The decrease in intensity of the OH-stretching vibration bands of the Brønsted acid sites was used to determine the coverage of the acid sites. The integral absorption coefficients of the CH-stretching vibrations of the adsorbed alkanes (2800−3000 cm^{-1}) were derived by relating the integral intensity to the gravimetric uptake. The integral intensities normalized by the absorption coefficient were used to derive the coverage/pressure dependencies of the individual adsorbate species.

Results

Sorption on H-FER. As seen in Figure 1, the heat of hexane sorption was constant up to a coverage of approximately 0.9 molecule/acid site. A similar behavior was found for the sorption of *n*-pentane. At higher loadings the heat values dropped, indicating that about 90% of the Brønsted acid sites of H-FER were accessible to *n*-hexane and *n*-pentane and that the alkanes were sorbed in a stoichiometry of 1 molecule/acid site. With propane the heat values started to drop at a coverage
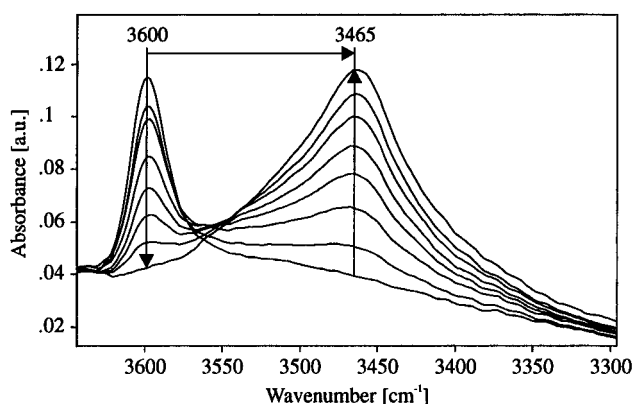
Figure 2. Infrared spectra of the OH-stretching vibrations of Brønsted acid sites of H-FER during adsorption of *n*-butane at 333 K. The lines correspond to increasing equilibrium pressure of *n*-butane.

TABLE 2: Heats of Sorption, Maximum Uptake Achieved at 13 mbar Alkane Partial Pressure and Henry's Constants at 333 K for Alkane Sorption on H-FER
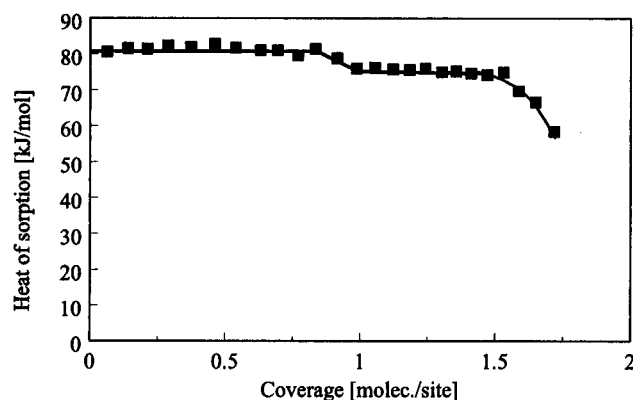
	ΔH_{ads} [kJ/mol]	max loading [mmol/g]	Henry's constant [mmol/(g atm)]
propane	−49	0.75	1.6×10^2
n-butane	−59	1.11	2.8×10^2
n-pentane	−69	0.56	8.2×10^2
n-hexane	−79	0.57	9.7×10^3

of about 1 molecule/acid site. The heat of *n*-butane sorption did not show a distinct decrease at a coverage of 1 molecule/acid site but stayed constant at a 1−2 kJ/mol lower value up to a coverage of more than 2 molecules/acid site.

The IR spectra of the activated sample showed a band at 3600 cm^{-1} attributed to the OH-stretching vibrations of the Brønsted acid sites. Upon sorption of *n*-hexane the integral intensity of this band decreased to approximately 10% of its original value when the pores were completely filled. This also indicates that about 90% of the acid sites of H-FER were accessible to *n*-hexane. The OH-stretching vibration band was broadened because of hydrogen bonding and shifted 130 cm^{-1} to lower wavenumbers, independent of the coverage. The band at 3600 cm^{-1} completely disappeared upon sorption of *n*-butane at sufficiently high partial pressures, indicating that (in contrast to *n*-hexane) all Brønsted acid sites of H-FER were accessible to *n*-butane (see Figure 2).

The heat of sorption increased linearly with the chain length of the alkane adsorbed with an increment of 10 kJ/mol per additional CH$_2$ group from 49 kJ/mol for propane to 79 kJ/mol for *n*-hexane. The uptake achieved with *n*-butane and propane exceeded markedly the uptake of *n*-pentane and *n*-hexane. This suggests that the pores of H-FER, accessible to *n*-butane and propane, are partially inaccessible to longer molecules. Consequently, the logarithm of the Henry's constants did not show a linear dependence on the chain length of the molecules sorbed as was frequently observed with other zeolite structures.[17] The values for the heat of sorption, the maximum uptake reached at an alkane partial pressure of about 13 mbar and Henry's constants are compiled in Table 2. Sorption of isobutane and isopentane was too low and equilibration too slow to allow for a determination of the heat of sorption or a sorption isotherm under the experimental conditions chosen.

Sorption on H-TON. Figure 3 shows the heat of hexane sorption on H-TON as a function of the coverage of the acid sites. The sorption enthalpy of ±81.5 kJ/mol was constant up to a coverage of 1 molecule/acid site. At higher coverages the heat of sorption showed an approximately 7 kJ/mol lower value and dropped markedly at a coverage of about 1.5 molecules/

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Figure 3. Differential heat of adsorption of *n*-hexane on H-TON as a function of the coverage at 333 K.

TABLE 3: Heat of Adsorption, Maximum Loading Achieved at ~13 mbar, and Henry's Constants (at 333 K) for Alkane Sorption on H-TON

	ΔH_{ads} [kJ/mol]	max loading [mmol/g]	Henry's constant [mmol/(g atm)]
propane	−49	0.24	4.4×10^1
n-butane	−60	0.49	4.1×10^2
n-pentane	−71	0.56	3.7×10^3
n-hexane	−81.5	0.56	2.6×10^4
isobutane	−47.5	0.10	1.9×10^1
isopentane	−59	0.18	2.0×10^2

acid site, indicating that all pores are filled at this loading. This suggests that all Brønsted acid sites of the H-TON sample used were accessible and that the alkanes are sorbed in a stoichiometry of 1 molecule/acid site.

IR spectroscopic measurements support this view. The integral intensity of the OH-stretching vibrations of the Brønsted acid sites at 3600 cm^{-1} decreased upon alkane sorption and disappeared fully at sufficiently high hydrocarbon partial pressures. This indicates that all Brønsted acid sites of H-TON are accessible. The band was broadened and shifted for 115−145 cm^{-1} to lower wavenumbers depending on the substance adsorbed. The wavenumber of this band was independent of the coverage, suggesting that the sorption stoichiometry does not change.

The sorption enthalpies, the maximum loading reached at an alkane partial pressure of 13 mbar, and Henry's constants are compiled in Table 3. The sorption enthalpy increased linearly with an increment of 11 kJ/mol per additional CH$_2$ group from 49 kJ/mol for propane to 81.5 kJ/mol for *n*-hexane. Isoalkanes showed about 12 kJ/mol lower values for the heat of sorption than the values determined for the corresponding *n*-alkanes. Henry's constants for the sorption of *n*-alkanes exhibited a logarithmic dependence on the carbon number of the molecules adsorbed. Again, Henry's constants for isoalkane sorption were significantly lower. As seen in Table 3, this resulted in a by far lower maximum uptake of the isoalkanes that could be achieved at 333 K and 13 mbar hydrocarbon partial pressure. This indicates that the pore size of ZSM-22 (0.44 × 0.55 nm) exerts constraints upon the sorption of isoalkanes.

Sorption on H-KFI. The heat of alkane sorption as a function of the coverage of H-KFI showed a unique trend. The heat of propane and *n*-butane sorption decreased with increasing coverage, the decrease being smaller for *n*-butane than for propane. The sorption enthalpies of *n*-pentane and *n*-hexane increased with coverage, and this increase was more pronounced with *n*-hexane (see Figure 4). The initial sorption enthalpy increased with increasing chain length of the alkanes with an increment of 3−5 kJ/mol per additional CH$_2$ group.
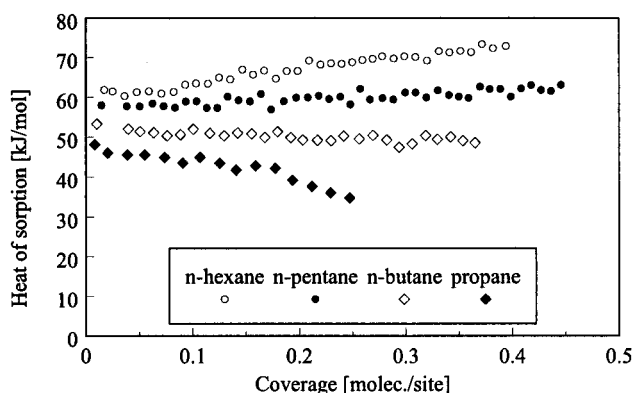
Figure 4. Differential heat of adsorption of *n*-alkanes on H-KFI as function of the coverage at 348 K.

TABLE 4: Initial Heats of Sorption, Maximum Uptake Achieved at 13 mbar Alkane Partial Pressure, and Henry's Constants at 348 K for Alkane Sorption on H-KFI

|	ΔH_{ads} [kJ/mol]	max loading [mmol/g]	Henry's constant [mmol/(g atm)]
propane	−47	0.56	2.3×10^2
n-butane	−52	1.19	4.3×10^2
n-pentane	−57	1.45	1.0×10^3
n-hexane	−60	1.29	2.1×10^3

The logarithm of Henry's constants rose linearly with the carbon number. Adsorption of isoalkanes was not observed under the experimental conditions chosen. The values for the initial heat of sorption, the maximum uptake achieved at about 13 mbar and 348 K, and Henry's constants at this temperature are compiled in Table 4. The isotherms were extrapolated to determine the saturation limit, suggesting a maximum uptake of 0.5−0.6 molecule/acid site depending on the sorbed substance.

The IR spectra of the activated sample exhibited two bands at 3608 and 3567 cm^{-1} attributed to OH-stretching vibrations. Only the band at 3608 cm^{-1} decreased in intensity upon interaction with the alkanes, while the band at 3567 cm^{-1} remained unaffected (see Figure 5). Therefore, the band at 3567 cm^{-1} is attributed to hydroxyl groups located off the large α or γ cages of KFI, which most probably protrude into the double six rings interconnecting the α cages. The close environment leads to a perturbation of the O−H bond, resulting in a lower wavenumber than for the hydroxyl groups pointing into the large cages of KFI (3608 cm^{-1}). Upon sorption of alkanes the band at 3608 cm^{-1} was broadened and red-shifted some 60−70 cm^{-1}. Since this shift is markedly lower than that observed with the other acidic zeolites investigated,[15] it suggests that the acid sites of H-KFI have a lower acid strength or the sorption is sterically constrained.

Discussion

By use of infrared spectroscopic measurements, it has been concluded previously for H-MFI, H-MOR, and H-FAU[15] that at low coverages alkanes are sorbed locally at the Brønsted acid sites of the zeolites. This is clearly confirmed by two observations reported here.

The first relates to the dependence of the heat of sorption on the coverage observed with H-TON. As shown in Figure 3, the heat of sorption was constant up to a coverage of 1 molecule/acid site and showed also a constant but approximately 7 kJ/mol lower value at higher coverages. This indicates that sorption on the acid sites is energetically favored over a delocalized sorption in the zeolite pores, the difference being in this case 7 kJ/mol. Only when all these favored sites were
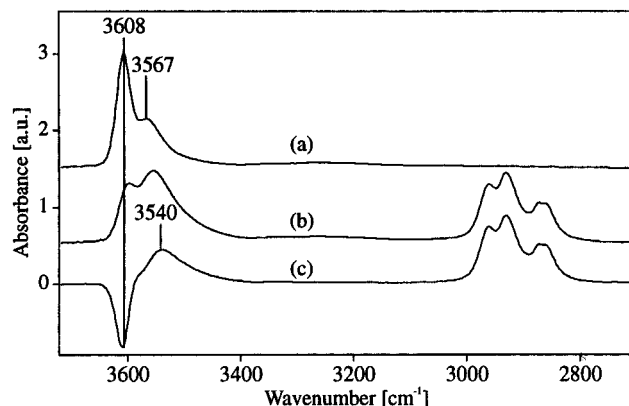
Figure 5. Infrared spectra of activated H-KFI (a), *n*-hexane sorbed on H-KFI at 348 K and an equilibrium pressure of 1 mbar (b), and the difference between the spectra a and b (c).
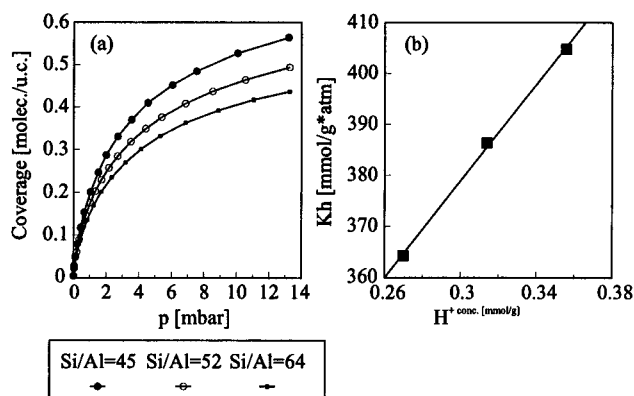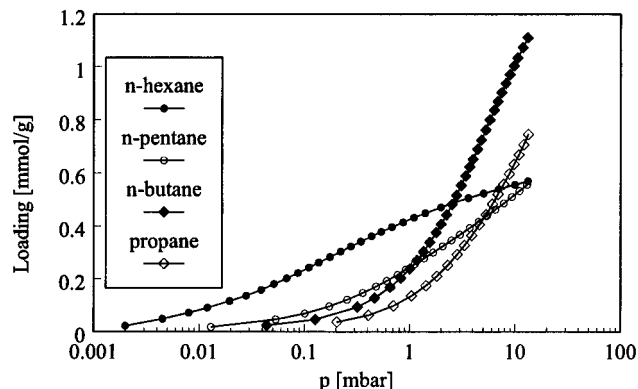

Figure 6. Adsorption isotherms of *n*-butane on H-TON with varying Si/Al ratio (a) and Henry's constants for *n*-butane sorption on H-TON at 333 K as function of the concentration of the acid sites (b).

covered alkanes were sorbed at other places in the pores (resulting in the lower heat of sorption). Since the step in the heat of adsorption was observed at a coverage of 1 molecule/ acid site, the possibility of an adsorption of two molecules at one acid site, as observed with H-MFI,[15] can be ruled out for H-TON. The heat of delocalized sorption was also constant until all pores were filled. Only then the heat value dropped significantly.

The second observation refers to the sorption isotherms of *n*-butane measured on three different H-TON samples. Figure 6a represents the uptake of *n*-butane achieved on H-TON samples with different Si/Al ratios (45, 52, and 64) as function of the *n*-butane partial pressure. In Figure 6b it is seen that Henry's constants for *n*-butane sorption on these three samples depended linearly on the concentration of the acid sites. This clearly shows that the loading at low pressures is directly related to the concentration of acid sites and not to the pore volume of the zeolite as it would be expected for delocalized sorption.

As with H-TON, the enthalpy for localized sorption on the acid sites of H-FER was constant up to a certain loading. It is striking, however, that the concentration at which the heat values started to decrease with increasing coverage differed significantly for the various *n*-alkanes studied. The sorption enthalpy of propane was constant up to a coverage of approximately 1 molecule/acid site, while the heat of *n*-hexane and *n*-pentane sorption dropped at a coverage of about 0.9 molecule/acid site. With *n*-butane a marked decrease of the heat of sorption was not observed up to a coverage of more than 2 molecules/acid site. At higher loadings the sorption enthalpy was only 1−2 kJ/mol lower than at zero filling (see Figure 1). In excellent agreement with IR spectroscopic results this suggests that 90%
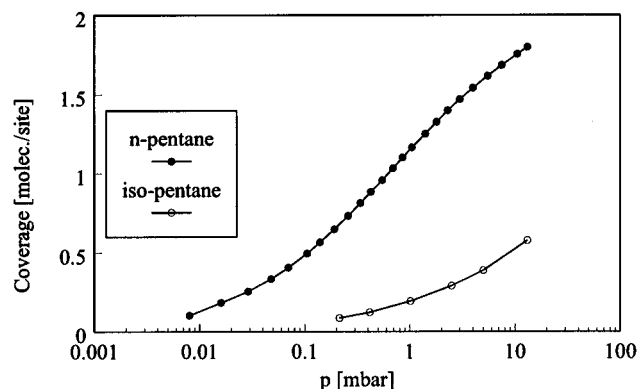

Figure 7. Adsorption isotherms of *n*-alkanes on H-FER at 333 K.

of the Brønsted acid sites of H-FER are accessible to *n*-hexane and *n*-pentane, while all sites can interact with *n*-butane and propane. Additional delocalized sorption leads to significantly lower sorption enthalpies for all alkanes except *n*-butane. This suggests an additional stabilization of *n*-butane molecules sorbed in a stoichiometry higher than 1 molecule/acid site or an energetically favored sorption complex that is not observed with shorter or longer molecules.

In Figure 2 the changes in the IR spectra of the OH bands of the Brønsted acid sites of H-FER during sorption of *n*-butane are shown. The band of the free hydroxyl groups (acid sites) at 3600 cm^{-1} is broadened and shifted to lower wavenumbers because of the perturbation of the O−H bond upon interaction with *n*-butane. The wavenumber of this band of perturbed OH groups was independent of the coverage. Since the perturbation of the hydroxyl group does not change with the coverage, we conclude that the sorption stoichiometry does not change. Thus, localized sorption of more than 1 molecule/acid site, as observed with H-MFI,[15] cannot account for the stabilization of the additional *n*-butane molecules.

The maximum loading with alkanes achieved at 13 mbar hydrocarbon partial pressure and 333 K also showed an unusual trend with the size of the alkane. The uptake deviated markedly from the expected trend (see Figure 7). At 13 mbar and 333 K it decreased in the order *n*-butane > propane > *n*-hexane ≥ *n*-pentane. At 13 mbar and 298 K *n*-hexane exhibited the lowest loading (0.66 mmol/g) compared to the smaller *n*-alkanes (1.54 mmol *n*-butane/g, 1.25 mmol propane/g, and 1.11 mmol *n*-pentane/g). These results indicate that a considerable fraction of the void volume of H-FER is not accessible to hexane, whereas it is accessible to *n*-butane, propane, and to a lesser extent *n*-pentane.

Such behavior is attributed to different accessibilities of the channel systems of H-FER. H-FER contains two straight elliptical channel types intersecting each other perpendicularly, one consisting of 10-member rings with a diameter of 0.54 × 0.42 nm, the other of 8-member rings with a diameter of 0.48 × 0.35 nm.[18] The length of an 8-ring channel between two intersections with the 10-ring channels is approximately 6 nm, corresponding well to the length of a *n*-butane molecule. This indicates that *n*-hexane is too long to be accommodated completely in the 8-ring channel sections. The sorption of *n*-pentane in these channels seems to be hindered but still possible to a certain extent. Since *n*-hexane interacted with 90% of the Brønsted acid sites, we conclude that most acid sites are located in the 10-ring channels and only 10% in the 8-ring channels. The decreasing sorption enthalpy of propane and pentane at elevated coverages suggests that sorption in the narrower 8-ring channels results in lower sorption enthalpies. Since such a significant decrease in the heat of sorption was
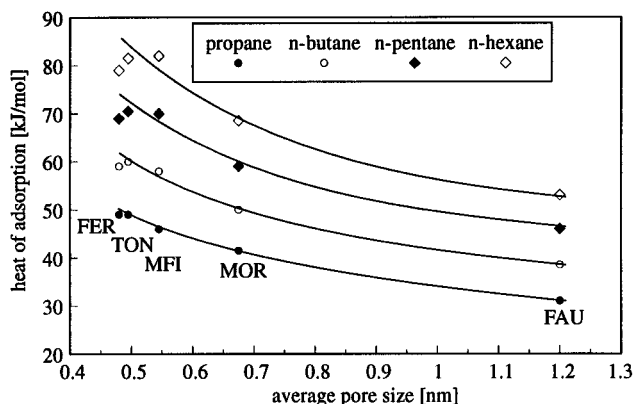
Figure 8. Adsorption isotherms of *n*-pentane and isopentane on H-TON at 333 K.

Figure 9. Differential heat of adsorption of *n*-hexane and isopentane on acidic zeolites as a function of the pore size. The pore diameter of H-FAU and H-KFI is represented as the diameter of the windows between the cages.

Figure 10. Differential heat of adsorption of *n*-hexane and isopentane on acidic zeolites as a function of the pore size. The pore diameter of H-FAU and H-KFI is represented as the diameter of the cages.

not observed for *n*-butane, it is speculated that an additional stabilization of the *n*-butane molecules due to the perfect fit into the section of the 8-ring channels between two intersections and/or sorbate–sorbate interactions in the intersections compensates for the lower heat of sorption in the smaller channels.
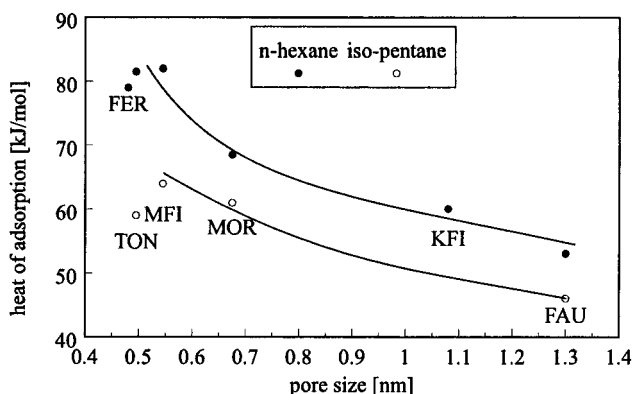
In contrast to the results on H-TON and H-FER, the heat of alkane sorption on H-KFI varied in a complex manner with the concentration of the sorbate. While the sorption enthalpy decreased with increasing loading of the zeolite for propane and *n*-butane, the sorption enthalpy increased for *n*-pentane and *n*-hexane. The decreasing heats of sorption with increasing coverage observed for propane and *n*-butane suggest that H-KFI contains sorption sites varying in strength and that strongest the sorption sites are covered first. The increasing sorption enthalpies of *n*-pentane and *n*-hexane indicate that this loss in heat of adsorption due to the sorption on weaker sites is compensated by sorbate–sorbate interactions that are more pronounced for longer hydrocarbons. Since the heat evolved due to sorbate–sorbate interactions increased with the square of the loading (indicated by a linear increase of the differential heat of sorption with increasing loading), it is concluded that an alkane molecule sorbed in the cages of H-KFI can only interact with one other molecule.[19]

Adsorption of isobutane and isopentane on H-KFI was not observed under the present experimental conditions. This clearly shows that the isoalkanes are too bulky to pass the diameter of 0.39 nm of the windows connecting the cages of KFI. It is striking, however, that the adsorption of isoalkanes is already constrained in the pores of H-TON (0.44 × 0.55 nm) (see Figure 8). This effect was even more pronounced with H-FER (0.42 × 0.54 nm). Since isoalkanes were easily adsorbed in H-MFI[15] (diameter of 0.53 × 0.56 nm for the straight channels), the results suggest that the limit in pore size for an unhindered adsorption of singly branched alkanes lies approximately at a pore diameter of 0.5 nm.

It has been proposed that the heat of adsorption is markedly influenced by the fit between the pore size and size of the molecule sorbed.[9–11] Such correlation suggests that an optimum situation between the hydrocarbons and the zeolite structure should exist and that this fit should depend on the shape of the molecule. Therefore, we compare the heat values reported in the present and an earlier study[15] as a function of the average pore diameter to explore the relation between structure and sorption thermodynamics. For zeolites with noncircular pore systems the average pore size is defined as the arithmetic mean of the pore dimensions. Zeolites with more than one pore system also have more than one average pore diameter. In the case of H-MFI the average pore diameter of the straight channels as the difference in size between the two-channel systems is

quite small. In the case of H-FER we used the pore diameter of the 10-ring pores because (i) all different *n*-alkane molecules could be accommodated in these pores and (ii) 90% of the favored sorption sites (i.e., the Brønsted acid sites) are located in these channels, as has been shown earlier. For zeolites consisting of interconnected cages such as H-FAU and H-KFI two different diameters could be taken, i.e., the diameter of the large cages and the diameter of the connecting windows. Figure 9 shows the dependence of the sorption enthalpy on the average pore size for *n*-hexane and isopentane, the pore size of H-FAU and H-KFI being represented as the diameter of the windows. The observed trend suggests the existence of a broad maximum that is found at larger pore diameters with isoalkanes. However, it was reported previously that alkanes sorb preferetially on acid sites located in the supercages of H-FAU.[15] This suggests that sorption of alkanes in H-FAU is determined by the local environment in the cages. Therefore, we compiled the dependence of the sorption enthalpy of *n*-hexane and isopentane on the average pore size in Figure 10, the pore size of H-FAU and H-KFI being represented as the diameter of the cages.

To a first degree, an increase in the heat of *n*-alkane sorption with decreasing pore size is established. Since the contribution of the acid sites to the heat of adsorption was similar for the various zeolites (only a difference of 4 kJ/mol was observed for zeolites differing in structure so drastically as H-MFI and H-FAU[19]), it is concluded that mainly structural parameters account for the trend observed. However, the sorption enthalpies of *n*-alkanes observed on H-FER deviated from this correlation, exhibiting somewhat lower values. This suggests that repulsion forces already start to play a considerable role at
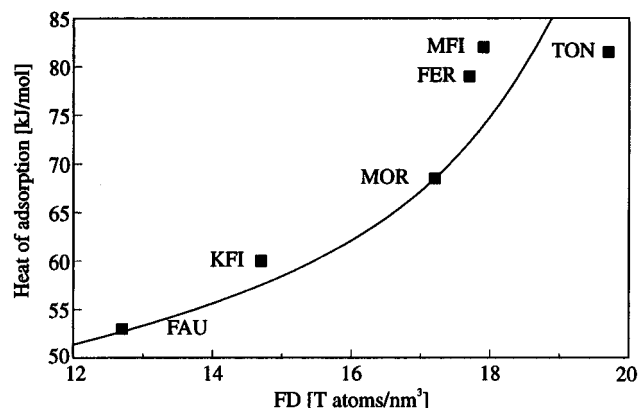
Figure 11. Differential heat of adsorption of *n*-hexane on acidic zeolites as a function of the framework density.

pore sizes smaller than 0.5 nm. With the bulkier isoalkanes this effect was even more pronounced.

It has been suggested that the heat of adsorption is a function of the framework density, which usually increases with decreasing pore size. As shown in Figure 11, the heat of *n*-hexane sorption exhibited a similar dependence on the framework density, as reported for ethane sorption on neutral molecular sieves by Stach et al.[12] Although more scatter of the data points was observed than for the correlation with the pore diameter, the trend indicates that higher framework densities lead to an increase in the strength of interaction between the zeolite lattice and sorbed alkanes.

Conclusions

Alkane molecules are locally sorbed on the Brønsted acid sites of zeolites at ambient temperatures as concluded from IR spectroscopic, calorimetric, and gravimetric measurements. It is inferred from these experiments that the Brønsted acid sites are energetically favored sorption sites in acidic zeolites and that the uptake with alkanes at low partial pressures is related to the concentration of acid sites present in the zeolite and not to the pore volume.

The chain length of the alkane molecules significantly influences not only the energetics but also the siting of sorbed alkanes. With H-FER the accessibility of the channel system consisting of 8-member rings differs substantially; when the carbon number of the molecules sorbed increases from 4 to 6, i.e., *n*-butane is sorbed readily, *n*-pentane sorption is hindered and *n*-hexane cannot be accommodated. These results indicate strong ordering in the sorbed state, i.e., that the length of the 8-ring channel between two intersections with the 10-ring

channels corresponds well to the length of a *n*-butane molecule. With H-KFI it can be shown that the heat evolved due to sorbate−sorbate interactions increases as the chain length of the alkane molecules increases. From the dependence of the heat of adsorption on the loading with alkanes, the number of molecules interacting with each other can be estimated.

Two effects of molecular sieving by the zeolites are clearly observed: (i) the limit in pore size for unhindered sorption of singly branched alkanes is about 0.5 nm; (ii) the heat of adsorption depends subtly on the fit between the size of the alkane molecule and the size of the zeolite pores, supporting earlier proposals of Derouane et al.[9] At pore sizes smaller than 0.5 nm repulsion forces lead to a decrease of the sorption enthalpies.

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