Characterization of the acid properties of [Al]-, [Ga]- and [Fe]-HZSM-5 by low-temperature FTIR spectroscopy of adsorbed dihydrogen and ethylbenzene disproportionation

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[Al]-, [Ga]- and [Fe]-HZSM-5 having closely similar Brønsted acid site densities were prepared. The low-temperature adsorption of H_2 and D_2 was studied by FTIR spectroscopy and the frequency shifts $\Delta\nu_{\mathrm{OH}}$ and $\Delta\nu_{\mathrm{HH}}$ ($\Delta\nu_{\mathrm{DD}}$) were measured and compared with corresponding frequency shifts observed for CO and N_2 probes. A linear correlation between $|\Delta\nu_{\mathrm{OH}}|^{1/2}$ which is proportional to the heat of formation ΔH_{B} of the H-bonded complex O–H $\cdots$ B (B representing the H-bond acceptor), and the proton affinities of the three probe molecules was found for [Al]-HZSM-5. The $\Delta\nu_{\mathrm{OH}}$-values measured for CO and H_2 (D_2) on the three isomorphously substituted zeolites suggested the following acid strength ranking: [Al]-HZSM-5 > [Ga]-HZSM-5 ≈ [Fe]-HZSM-5. This sequence is clearly reflected in the relative activities of the materials for the acid-catalyzed disproportionation of ethylbenzene.

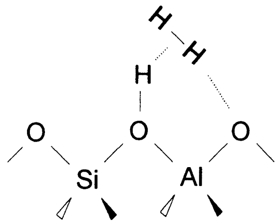
Keywords: Brønsted acid strength, [Al]-HZSM-5, [Ga]-HZSM-5, [Fe]-HZSM-5, H_2-adsorption, CO-adsorption, FTIR spectroscopy, ethylbenzene disproportionation

1. Introduction

Many industrially important acid-catalyzed reactions such as the selective transformations of hydrocarbons and their derivatives are based on the presence of Brønsted acid sites in the H-forms of zeolitic materials. Therefore, the acidity of zeolites has been extensively studied by a variety of techniques [1,2]. Infrared spectroscopy in combination with low-temperature adsorption of small probe molecules is one very promising approach toward the determination of the relative acid strength of different solid materials. Carbon monoxide has been used as a probe molecule most frequently in the past [3–12]. Recently, the homonuclear diatomic molecules dinitrogen [13–16], dioxygen [17] and dihydrogen [17–23] are also considered as possible probe molecules and their specific interaction with acidic hydroxyl groups in various zeolites and other oxide materials has been demonstrated by infrared spectroscopy. These molecules undergo 1 : 1 H-bond type interactions with the acidic OH groups and induce characteristic modifications of the infrared spectra of both the O–H oscillator and the diatomic probe molecule. The low-frequency shifts $\Delta\nu_{\mathrm{OH}}$ of the perturbed relative to the unperturbed OH groups can be considered as a measure of the enthalpy of interaction ΔH of the O–H $\cdots$ B complex (B representing the H-bond acceptor probe molecule).

The infrared silent stretching mode of homonuclear diatomic probes has been shown to be activated by the intermolecular interaction with OH groups [13–23] and to suffer frequency shifts relative to the Raman band of the free molecule. The extents of these frequency shifts are again determined by the enthalpy of interaction in the surface complex.

Density functional investigations have suggested that CO and N_2 form 1 : 1 complexes with acidic OH groups, in which the probe is bonded in an end-on configuration [15,24]. The CO molecule is forming a σ-donor bond via the 5σ orbital at the C-atom. In contrast, experimental data [17] and theoretical calculations [22,25] are in favor of a side-on configuration in the case of H_2 in which one H-atom is simultaneously interacting with a neighboring lattice oxygen atom:



The strength of acid sites in a zeolite of a given framework topology can be modified by isomorphous substitution. For silicates with the framework topology of zeolite ZSM-5 (MFI-structure), isomorphous substitution can be conveniently achieved by replacing the aluminum source in the synthesis gel by other trivalent

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metal cations, i.e. gallium or iron [26–30]. Based on the position of the O–H stretching frequency [27,28], on thermal desorption of ammonia [27,31], on quantum chemical calculations [24,31] as well as on catalytic test reactions [31], it was concluded that the strength of the acid sites decreased in the sequence [Al]-HZSM-5 > [Ga]-HZSM-5 > [Fe]-HZSM-5. In previous reports, we have supported this sequence by infrared spectroscopy using CO as a probe molecule [8] for the [Al]- and [Ga]-forms and by a density functional model cluster study [24]. In the present contribution, we report on the adsorption of H_2 and D_2 as probe molecules on the series of [Al]-, [Ga]- and [Fe]-ZSM-5 as studied by FTIR-spectroscopy. The results will be compared with those obtained with CO and N_2 probe molecules and correlated with the activity for the acid-catalyzed disproportionation of ethylbenzene of these materials having approximately the same densities of Brønsted acid sites.

2. Experimental

2.1. Zeolite synthesis and characterization

Aluminum-, gallium, and ironsilicates with the structure of zeolite ZSM-5 (MFI-topology) and comparable $n_{Si}/n_{Me^{3+}}$ ratios (around 22) were synthesized from gels of the molar composition $48SiO_2{:}Me_2O_3{:}7.3TPABr{:}15.3Na_2O{:}8.7H_2SO_4{:}1350H_2O$. $Al(NO_3)_3{\cdot}9H_2O$, $Ga_2(SO_4)_3{\cdot}7H_2O$ and $Fe(NO_3)_3{\cdot}9H_2O$ were used as sources for the trivalent metal ions, respectively. Tetrapropylammoniumbromide (TPABr) was used as the template and sodium waterglass solution (8.8 wt% Na_2O, 28.5 wt% SiO_2) was used as silica source. The gels were crystallized for 4 days at 433 K under continuous stirring in stainless steel autoclaves ($V \approx 250$ cm^3). The resulting crystalline products were washed with water, dried overnight at 393 K and afterwards heated with 5 K/min to 773 K in a flow of dry nitrogen. At this temperature, air was mixed to the nitrogen flow to achieve complete combustion of the organic template occluded in the zeolite pores. The resulting materials were then ion exchanged three times with a larger surplus of a 1 N aqueous solution in order to obtain the ammonium forms of the metallosilicates. All synthesized materials were checked by X-ray powder diffraction for the absence of other crystalline or amorphous impurities.

Bulk chemical analysis gave n_{Si}/n_{Me} ratios of 23.0, 25.5 and 20.0 for the alumino-, the iron- and the gallosilicate, respectively. The corresponding values from ^{29}Si-MAS-NMR were 23 and 25 for the alumino- and the gallosilicate [8], respectively, suggesting that, while all Al^{3+} was incorporated in the lattice of [Al]-HZSM-5 consistent with ^{27}Al-MAS-NMR, some of the Ga^{3+} in [Ga]-HZSM-5 was on extra lattice positions. This was also confirmed by temperature-programmed desorption of ammonia (TPDA), which gave n_{Si}/n_{Me} ratios of 23.8 and 29.5, respectively. In conclusion, the densities of Brønsted sites in the alumino- and gallosilicate are close although not identical.

In the case of the ferrisilicate, the framework n_{Si}/n_{Fe} ratio could not be determined by ^{29}Si-MAS-NMR due to the quadrupolar nature of the iron. From temperature-programmed desorption of ammonia, however, a n_{Si}/n_{Fe} ratio of 35 could be deduced which indicates that a non-negligible amount of extra-framework iron is present in [Fe]-HZSM-5. Hence, this material possesses a lower densitiy of Brønsted acid sites than the [Al]- and [Ga]-HZSM-5 samples. The presence of certain amounts of extra-framework iron in ferrisilicates has been repeatedly reported in the literature [33,34].

2.2. Infrared spectroscopy

For transmission infrared spectroscopy the samples were ground and pressed into self-supporting wafers, having a typical weight of 10–15 mg/cm^2. The in situ pretreatment consisted in heating at 673 K in flowing N_2 ($v \approx 2$ dm^3/h; heating rate $\beta = 10$ K/min) for 16 h, followed by evacuation ($p < 2 \times 10^{-5}$ hPa) at 673 K for 4 h. The wafer was moved to the low-temperature infrared cell [32] and cooled with liquid nitrogen to approximately 85 K prior to adsorption of the probe molecules. The spectra were recorded with a Bruker IFS 66 FTIR spectrometer by accumulating 128 scans, operating at a spectral resolution of 1 cm^{-1}.

Nitrogen, hydrogen and carbon monoxide were supplied by Linde. Hydrogen and nitrogen with a nominal purity of 99.999% were further purified and dried by passing through an Oxisorb cartridge. Hydrogen and deuterium, the latter provided by Messer-Griesheim with a nominal purity of 99.7%, were passed through a liquid nitrogen cooling trap prior to adsorption. Carbon monoxide (nominal purity 99.997%) was used without further purification.

2.3. Catalytic testing

The catalytic experiments were conducted in a flow-type apparatus with a fixed-bed reactor under atmospheric pressure. Prior to the catalytic experiments, the catalysts were thermally treated in situ at 623 K for 16 h in a purge of dry nitrogen to obtain the H^+-forms. The following reaction conditions were used to study the disproportionation of ethylbenzene (EB): $T_{reaction} = 523$ K; modified residence time $W/F_{EB} = 600$ g h/mol; dry mass of catalyst: $m_{cat} = 0.3$ g; $p_{EB} = 1.3$ kPa; carrier gas: nitrogen. The conversion of ethylbenzene was followed in dependence of time-on-stream by on-line sampling and gas chromatographic analysis of the reaction products.

3. Results and discussion

3.1. Hydroxyl stretching vibrations of free OH groups

The FTIR spectra of the hydroxyl stretching region of the zeolites prior to adsorption of hydrogen were recorded at 85 K after pretreatment with nitrogen and subsequent evacuation at 673 K. The bands at 3745 cm^{-1} are assigned to isolated silanol OH groups that are located on the external surface of the zeolite crystallites [5,10]. The bands at lower frequencies are attributed to the OH stretching modes of the acidic framework OH groups as reported in the literature [5–7,10]. The band positions at 3618, 3622 and 3637 cm^{-1} of these OH groups clearly shift to higher frequencies in the series [Al]-HZSM-5 < [Ga]-HZSM-5 < [Fe]-HZSM-5. The same trend had been observed by Chu and Chang [27] and by Post et al. [28]. The former authors have correlated the O–H stretching frequencies for the same family of isomorphously substituted zeolites including in addi-

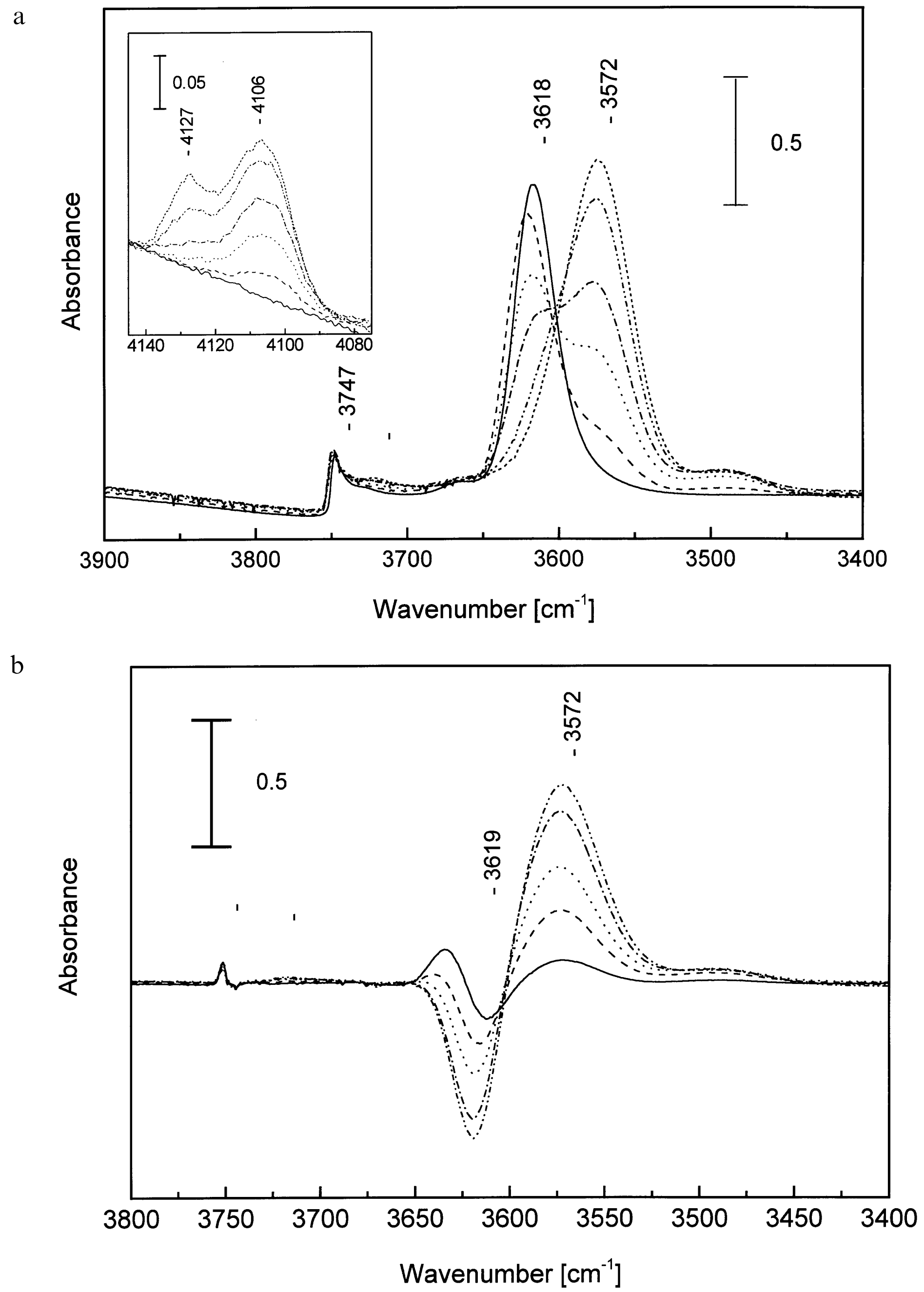

Figure 1. (a) Low-temperature adsorption of hydrogen: Infrared spectra of the OH and HH region (inset) of [Al]-HZSM-5 at 85 K: (——) vacuum, (- - -) 5.0 hPa H_2, (· · ·) 20 hPa H_2, (-·-·-) 50 hPa H_2, (-··-··-) 200 hPa H_2, (- - - -) 500 hPa H_2. (b) Corresponding difference spectra after subtraction of the background spectrum of the zeolite.

tion [B]-HZSM-5 with the maximum temperature of thermal desorption spectra of ammonia. They concluded that the Brønsted acid strength decreased in the reverse order to the increase of the O–H stretching frequency.

3.2. Adsorption of dihydrogen

Figure 1a shows the spectra of [Al]-HZSM-5 at 88 K under vacuum and in presence of hydrogen at different equilibrium pressures. After dosing a small increment of hydrogen the initial OH band at 3618 cm^{-1} is slightly shifted upwards by ca. 2 cm^{-1}. As reported by Wakabayashi et al. [17], this shift is observed when the interaction between OH groups and gas molecules is weak or negligible. However, an unequivocal interpretation of this effect is not yet available. Two explanations were discussed: (i) The sample temperature might be lowered by introducing the gas which acts as a heat carrier between the sample and the cooled cell [35]. This, however, is in contrast with the observation, that the sample temperature must be lowered by some 110 K to induce a frequency shift of 2 cm^{-1} [36]. (ii) The second possible explanation is that the frequency of the vibrational–rotational transitions is increased by a collision effect. This behavior has been reported for molecules in the gas phase by Letokhov [37], but was found to be pressure dependent and to cause much lower frequency shifts than the pressure independent effect observed here.

The spectra of figure 1a clearly show that the intensity of the band at 3618 cm^{-1} of the unperturbed acidic OH groups continuously decreases as the H_2 equilibrium pressure is increased. A new band at 3572 cm^{-1} grows in simultaneously. The occurrence of an isosbestic point and the inspection of the difference spectra in figure 1b suggest that this band is to be attributed to the O–H stretching band of the acidic OH groups being perturbed by interaction with the H_2 molecule. In fact, saturation isotherms are obtained when the decrease of the integral intensity ΔI_{OH} of the initial band at 3618 cm^{-1} or the increase in integral intensities I_{OH} of the shifted O–H stretching band at 3572 cm^{-1} or of the H–H stretching band I_{HH} of the adsorbed dihydrogen molecule at 4106 cm^{-1} (see below) is plotted versus the equilibrium H_2 pressure. A linear relation is found between ΔI_{OH} and I_{OH}, which supports the assignment given above.

The band of the perturbed hydroxyl groups, in addition to the frequency shift, has an increased half-width and an increased integral intensity at saturation as compared to the band at 3618 cm^{-1} of unperturbed OH groups. These effects are characteristic of H-bonding interactions.

Consequently, this intermolecular interaction with acidic OH groups is expected to also affect the vibrational behavior of the H_2 molecule. The spectra in the H–H stretching region of the H_2 molecule are shown in the inset of figure 1a. The H–H stretching mode becomes infrared active due to the polarization of the molecule induced by adsorption and appears at 4106 cm^{-1}. The frequency is shifted to lower wavenumbers relative to the Raman frequency at 4162 cm^{-1} [39] of the infrared inactive gas phase molecule. This band becomes detectable even at the lowest hydrogen pressures whereas a second band at 4127 cm^{-1} grows in only at higher pressures. Inspection of the isotherms in figure 2 clearly shows the

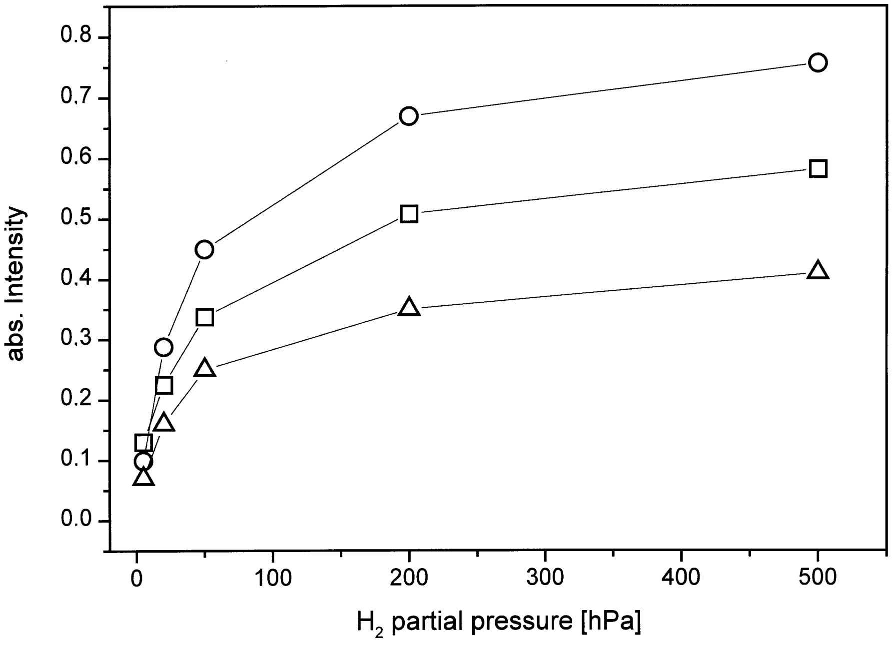

Figure 2. Adsorption isotherms for H_2 adsorption on [Al]-HZSM-5 at approximately 85 K: (○) ΔI_{OH}, (□) I_{OH}, (△) I_{HH}.

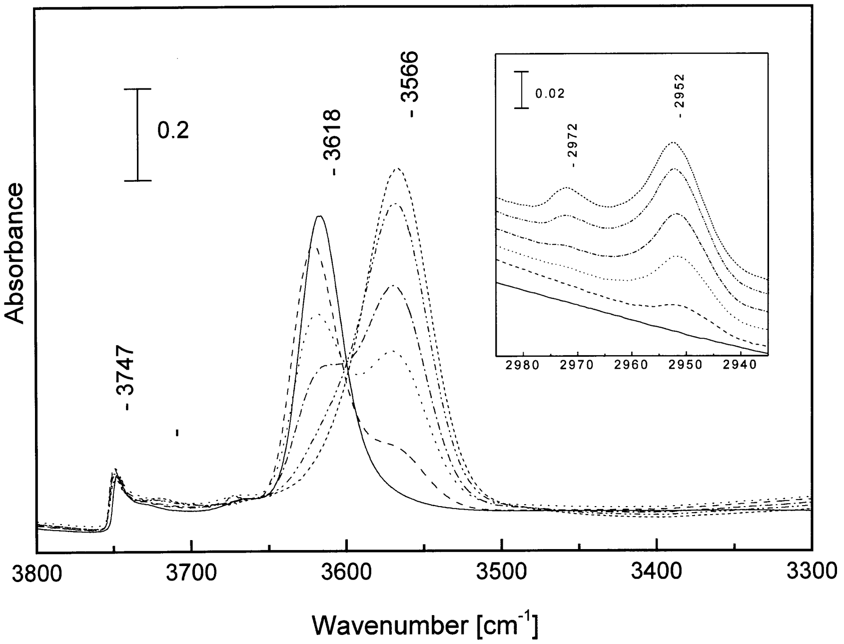

Figure 3. Low-temperature adsorption of deuterium: Infrared spectra of the OH and DD region (inset) of [Al]-HZSM-5 at 85 K: (——) vacuum, (- - -) 5.0 hPa D_2, (· · ·) 20 hPa D_2, (-·-·-) 50 hPa D_2, (-··-··) 200 hPa D_2, (- - - -) and 500 hPa D_2.

direct relation between the acidic hydroxyl group and the band at 4106 m^{-1}. Therefore the band at 4106 cm^{-1} is attributed to a hydrogen molecule bonded to an acidic hydroxyl group. Similar band positions have been reported in the literature for several zeolites and molecular sieves including [Al]-HZSM-5 [17,18,23]. The position of the second high-frequency H–H stretching mode at 4127 cm^{-1} coincides with that reported by Garrone et al. [22] and attributed to H_2 interacting with silanol groups on silica surfaces. In the present case, however, the silanol band at 3745 cm^{-1} remains practically unperturbed. It is therefore inferred that the band at 4127 cm^{-1} may be due to weakly adsorbed hydrogen held by van der Waals forces in the zeolite micropores.

The observations described above are fully supported by the FTIR spectra measured during D_2 adsorption as shown in figure 3. The O–H stretching band of the perturbed OH groups appears at 3566 cm^{-1}, its low frequency shift being slightly greater than that for H_2 adsorption. This effect is presumably due to the higher mass of D_2. As shown in the inset of figure 3 two bands at 2952 and 2972 cm^{-1} appear in the D–D stretching region that correspond to the D_2 molecules interacting with the acidic OH groups and to weakly adsorbed D_2, respectively. The experimental frequency ratios $\nu_{\mathrm{HH}}/\nu_{\mathrm{DD}}$ are 1.391 and 1.389, respectively, and are almost identical to the theoretical value of 1.41 in the harmonic oscillator approximation.

The spectral behavior for the H_2 adsorption on the gallo- and ferrisilicate is qualitatively identical to that observed for the aluminosilicate. Therefore the corresponding spectra are not shown. The observed frequency shifts are summarized in table 1 and compared with the corresponding frequency shifts that were measured with CO and N_2 as probe molecules. The $\Delta\nu_{\mathrm{OH}}$ frequency shifts induced by CO and H_2 (or D_2) give the sequence [Al]-HZSM-5 > [Ga]-HZSM-5 ≈ [Fe]-HZSM-5, and the same trends are seen for the shifts of the stretching modes of the probe molecules. It is thus inferred that the acid strength of the aluminosilicate is higher than that of

Table 1
Summary of experimental infrared frequency shifts for adsorption of CO, N_2, H_2 and D_2 on [Al]-, [Ga]- and [Fe]-HZSM-5

	IR-frequency / acidic hydroxyl groups (cm^{-1})					IR-frequency shift / probe molecules (cm^{-1})			
	ν_{initial}	$\Delta\nu_{+\mathrm{CO}}$	$\Delta\nu_{+\mathrm{N}_2}$	$\Delta\nu_{+\mathrm{H}_2}$	$\Delta\nu_{+\mathrm{D}_2}$	$\Delta\nu$(C–O)	$\Delta\nu$(N–N)	$\Delta\nu$(H–H)	$\Delta\nu$(D–D)
[Al]-HZSM-5	3618	−313 [a]	−109 [b]	−45	−52	+32 [a]	+2 [b]	−55	−40
[Ga]-HZSM-5	3622	−291 [a]		−35	−41	+29 [a]		−50	−37
[Fe]-HZSM-5	3637	−289		−37	−44			−50	−33

[a] Data from ref. [8].

[b] Data from ref. [15].

the other two zeolites, while that of these latter materials must be very closely the same. It should be noted that Zecchina et al. [38] very recently reported frequency shifts $\Delta\nu_{\mathrm{OH}}$ of -270 and $-100\ \mathrm{cm}^{-1}$ when they adsorbed CO and N_2, respectively, on a ferrisilicate with a Si/Fe ratio of 50.

It is well known for H-bonded systems that the square root of the frequency shift induced by interaction of a base B with, e.g., an O–H group (O–H $\cdots$ B) is proportional to the hydrogen bond strength or enthalpy of formation of the H-bond ΔH_{B} [40]:

$$|\Delta\nu_{\mathrm{OH}}|^{1/2} \sim \Delta H_{\mathrm{B}}\,. \tag{1}$$

This relation has been verified for the adsorption of H_2 on a series of molecular sieves by Makarova et al. [23], and Wakabayashi et al [17] have shown that $|\Delta\nu_{\mathrm{OH}}|^{1/2}$ correlates linearly with the proton affinity $\mathrm{PA_B}$ of several noble gases, H_2, O_2 and N_2 when they are interacting with acidic OH groups in H-mordenite:

$$|\Delta\nu_{\mathrm{OH}}|^{1/2} \sim a\mathrm{PA_B} + b\,. \tag{2}$$

As a first approximation, it was proposed that this relation should hold when the adsorbent zeolite was the same. One may thus expect an analogous linear correlation to be valid for the isomorphously substituted ZSM-5 zeolites studied in the present work when the square-roots of the $\Delta\nu_{\mathrm{OH}}$ values reported in table 1 for H_2, N_2 and CO probe molecules are correlated with their respective PA values which are 424, 477 and 598 kJ/mol [3]. As shown in figure 4, a linear correlation is indeed obtained for [Al]-HZSM-5. The data for H_2 and CO probes adsorbed on the gallo- and ferrisilicate fall below the correlation line for the aluminosilicate consistent with the proposed higher acid strength (higher ΔH_{B}) of the latter, although the difference seems to be small. A difference in the acid strength between the gallo- and ferrisilicate cannot be detected by this spectroscopic approach.

3.3. Catalytic testing

The results of the catalytic tests are summarized in figure 5. It can be seen that the conversion of ethylbenzene slightly decreases with time-on-stream and reaches an almost stable value after several hours. With all catalysts, the acid-catalyzed disproportionation of ethylbenzene to benzene and the three diethylbenzene isomers is the sole reaction. Under the assumption that the densities of the Brønsted-acid sites in the Al-, Ga- and Fe-silicates are comparable (similar $n_{\mathrm{Si}}/n_{\mathrm{Me}}$ ratios), it can be concluded that the strength of the acid sites declines in the sequence [A]-HZSM-5 > [Ga]-HZSM-5 ⩾ [Fe]-HZSM-5, which is, in principle, in agreement with the results of the characterization by IR-spectroscopy. It must, however, be admitted that some of the iron in the ferrisilicate is located in extra-lattice positions, so that the site density of the Fe-silicate is in fact somewhat lower than in the other two silicates.

4. Conclusions

Consistent with earlier reports [17,23], it is shown that dihydrogen can be considered as a convenient probe molecule for infrared studies of the Brønsted acidity of solid acids, particularly of zeolites. Application of H_2 for the characterization of [Al]-, [Ga]- and [Fe]-HZSM-5 shows that the Brønsted acid strength follows the sequence [Al]-HZSM-5 > [Ga]-HZSM-5 ≈ [Fe]-HZSM-5, this trend being supported by the result obtained with CO as a probe.

The catalytic activity of the three materials for the acid-catalyzed disproportionation of ethylbenzene principally follows the same trends, although the steady state activity of ferrisilicate seems to be slightly smaller than that of gallosilicate. This, however, may also be due to a smaller site density in this material.

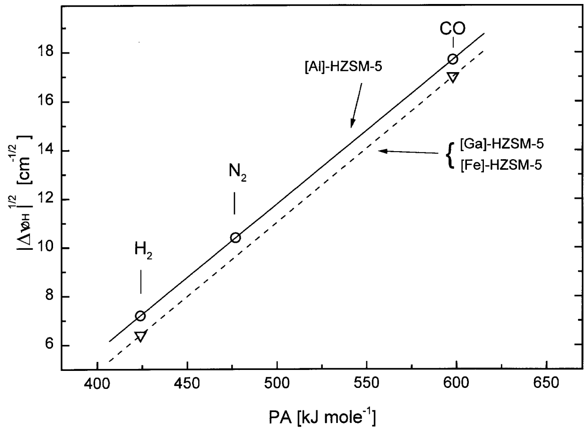

Figure 4. Correlation of $|\Delta\nu_{\mathrm{OH}}|^{1/2}$ and the proton affinities PA of H_2, N_2 and CO.

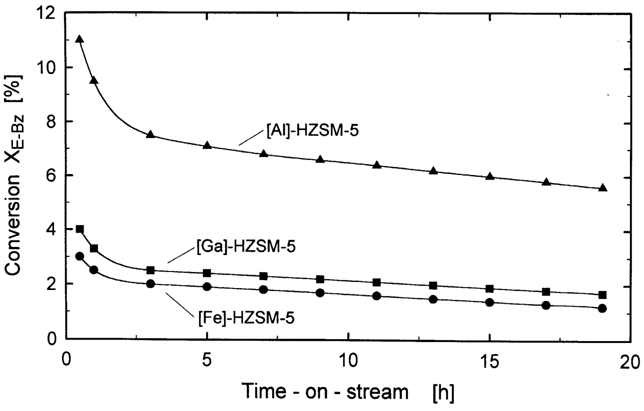

Figure 5. Conversion vs. time-on-stream for the disproportionation of ethylbenzene on [Al]-, [Ga]- and [Fe]-HZSM-5 (conditions see experimental section).

Our previous density functional model cluster studies [24] had predicted significantly larger differences between the [Ga]- and [Fe]-forms of the HZSM-5 zeolites as compared to the present experimental result. This discrepancy will presumably be removed when more realistic cluster models are being used for the theoretical studies.

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