Characterization of acid properties of [Al]- and [Ga]-HZSM-5 zeolites by low temperature Fourier transform infrared spectroscopy of adsorbed carbon monoxide

Ibad Mirsojew [a,1], Stefan Ernst [b], Jens Weitkamp [b] and Helmut Knözinger [a,2]

[a] *Institut für Physikalische Chemie, Universität München, Sophienstrasse 11,*
80333 Munich, Germany
[b] *Institut für Technische Chemie I, Universität Stuttgart, Pfaffenwaldring 55,*
70550 Stuttgart, Germany

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[Al]- and [Ga]-HZSM-5 having closely similar acid site densities were prepared. Temperature-programmed desorption of ammonia (TPDA) proved the known acid strength sequence: [Al] > [Ga]. Frequency shifts of the OH stretching mode to lower frequencies were induced upon CO adsorption at 77 K due to OH ··· CO H-bonding interactions. These frequency shifts are a measure of the H-bond donor strength of the OH groups and hence, of their acidic strength. The observed shifts of 313 and 282 cm^{-1} for the [Al]- and [Ga]-silicate, respectively, clearly reflect their relative acid strength. [Ga]-HZSM-5 develops an acid strength similar to that found for HNaY at high exchange levels. Evidence is presented for an intrinsic heterogeneity of acid properties of the acidic hydroxyls probably caused by inhomogeneous distributions of the trivalent cations in the framework.

Keywords: Acidity; [Al]-HZSM-5; [Ga]-HZSM-5; HNaY; CO-adsorption; FTIR-spectroscopy

1. Introduction

One of the major fields of application of zeolites is their use as acid catalysts in petroleum refining and petrochemistry. Characterization of zeolite acidity therefore plays an important role in tailoring the catalytic properties of zeolites and

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[1] On leave from Institute of Petroleum and Chemistry, M. Azizbekov, Baku, Azerbeidjan.
[2] To whom correspondence should be addressed.

related molecular sieves. The term "acidity" usually covers the nature (Brønsted versus Lewis acidity), density, and strength (or strength distribution) of the acid sites [1]. Each of these properties can be characterized individually by carefully selected experimental techniques. Among these, infrared spectroscopy of adsorbed basic probe molecules, such as e.g. ammonia and pyridine has played a dominant role in characterizing surface acidity of catalysts in general [1,2]. These probe molecules are strong bases and they are consequently not very specific regarding differences in Brønsted acid strength of OH-groups. The adsorption of carbon monoxide at low temperature has therefore been proposed as a powerful alternative for the characterization of acid sites on solid catalyst surfaces [3–5]. CO undergoes H-bonding interactions with surface hydroxyl groups with formation of 1 : 1 $OH \cdots CO$ complexes. This intermolecular interaction leads to characteristic low-frequency shifts of the O–H stretching mode and high-frequency shifts of the C–O stretching mode depending selectively on the strength of the interaction. This has been demonstrated for a variety of binary oxides [3,4,6,7] and zeolitic and other molecular sieve materials [8–12]. These investigations have clearly shown that the observed frequency shifts $\Delta\nu_{OH}$ and $\Delta\nu_{CO}$ can be related to the protonic (or Brønsted) acidity of the materials under investigation. Thus, for SiO_2 typical $\Delta\nu_{OH}$ values of 90 cm^{-1} have been reported [6,7], while shifts of more than 300 cm^{-1} have been observed for HZSM-5 type zeolites [8,9,12]. Kubelková et al. [9] found a correlation between $\Delta\nu_{OH}$ and the proton affinities of the corresponding OH groups the latter decreasing in the sequence $SiOH > AlOH \geqslant POH > Si(OH)Al$. Chevreau et al. [13] were able to linearly correlate $\Delta\nu_{OH}$ values induced by CO and C_2H_4 on a series of dealuminated zeolites and to establish an H_0 scale for the corresponding OH groups based on H_0 values reported by Umansky et al. [14] for the same type of materials.

It is well known that the strength of acid sites in a zeolite of a given framework topology can be varied by isomorphous substitution. In the case of silicates with the framework topology of zeolite ZSM-5 (MFI-structure), isomorphous substitution is conveniently achieved by replacing the aluminium source in the synthesis gel by other trivalent metals, i.e. gallium or iron [15–18]. It has been shown by a shift of the OH-bands in the infrared spectra [16,17], by temperature-programmed desorption of ammonia TPDA [15] and by catalytic test reactions [17,18] that the strength of the acid sites decreases in the sequence [Al]-HZSM-5 > [Ga]-HZSM-5. In this paper, we report a first systematic characterization of alumino- and gallosilicates with the MFI-topology by infrared spectroscopy combined with low temperature CO-adsorption. The zeolites were synthesized such that they nominally contained the same concentration of trivalent metal ions with the goal to investigate a series of zeolites having the same topology and acid site density, but different acid strength. For the characterization of the acid properties of the zeolite preparations under investigation and for comparison with existing literature data, we also report TPDA results.

2. Experimental

2.1. ZEOLITE SYNTHESIS

Alumino- and gallosilicates with the MFI-topology and comparable $n_{Si}/n_{Me^{3+}}$ ratios were synthesized from gels of the molar composition 48 SiO_2 : Me_2O_3 : 7.3 TPABr: 15.3 Na_2O : 8.7 H_2SO_4 : 1350 H_2O. $Al(NO_3)_3 \cdot 9H_2O$ and $Ga_2(SO_4)_3 \cdot 7H_2O$ were used as sources for the trivalent metal ions, respectively. Tetrapropylammoniumbromide (TPABr) was used as the template and sodium waterglass (8.8 wt% Na_2O, 28.5 wt% SiO_2, rest: water) 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 to 773 K at 5 K/min 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 than ion exchanged three times with a large surplus of a NH_4Cl-solution in order to obtain the ammonium forms of the metallosilicates.

2.2. ZEOLITE CHARACTERIZATION

The materials were characterized by X-ray powder diffraction, chemical analysis (AAS/ICP), ^{27}Al- and ^{29}Si-MAS-NMR-spectroscopy (Bruker MSL-400), and temperature programmed desorption of ammonia (TPDA). For the latter purpose, the ammonium forms of the metallosilicates were first heated to 773 K with a rate of 5 K/min in a flow of dry nitrogen, kept at this temperature for 3 h and afterwards cooled to 373 K. At this temperature, the samples were purged first with pure ammonia for 30 min and then with pure nitrogen for 16 h, to desorb physically adsorbed ammonia. For the TPDA-experiment, the sample was then heated with 5 K/min to 823 K and the evolved ammonia was monitored by mass spectroscopy.

2.3. INFRARED SPECTROSCOPY

For transmission infrared spectroscopy, the materials were ground and pressed (300 bar) into self-supporting wafers having a weight of typically 10–15 mg/cm^2. The low-temperature infrared transmission cell has been described previously [19]. The cell was connected to a reactor in which in situ pretreatments at elevated temperatures could be carried out. Standard pretreatments of the wafers consisted in heating at 673 K in flowing N_2 for 16 h followed by evacuation (2×10^{-5} mbar) at 673 K for varying periods of time and cooling to liquid N_2 temperature prior to dosing CO in small increments starting at an equilibrium pressure of typically 0.1 mbar. The infrared spectra were recorded at a spectral resolution of 2 cm^{-1} on a Bruker IFS 66 Fourier transform spectrometer.

The N_2 gas was from Linde and had a nominal purity of 99.999%. It was further purified and dried by passing it through an Oxisorb cartridge. The CO gas was also from Linde and had a nominal purity of 99.997%. CO was used without further purification.

3. Results and discussion

3.1. STRUCTURAL CHARACTERIZATION

X-ray powder diffraction revealed that the synthesized and modified metallosilicates had the MFI-topology and were of high crystallinity.

The results of bulk chemical analyses are as follows: [Al]-HZSM-5: $n_{Si}/n_{Al} = 23.0$ and [Ga]-ZSM-5: $n_{Si}/n_{Ga} = 20.0$ in good agreement with $n_{Si}/n_{Me^{3+}} = 24$ in the synthesis gels.

The framework $n_{Si}/n_{Me^{3+}}$-ratios of the alumino- and the gallosilicates were determined by ^{29}Si-MAS-NMR-spectroscopy after calcination. They amount to $n_{Si}/n_{Al} = 23.0$ for the aluminosilicate and $n_{Si}/n_{Ga} = 25$ for the gallosilicate. If the latter figure is compared to the result of the bulk chemical analysis, one is tempted to assume that some of the gallium present in [Ga]-HZSM-5 is on extra-lattice positions. In [Al]-HZSM-5, however, all aluminium is supposed to be in tetrahedral lattice positions. This is also confirmed by the absence of a band for octahedrally coordinated aluminium in the ^{27}Al-MAS-NMR-spectrum and the lack of carbonyl infrared bands characteristic of $Al^{3+} \leftarrow CO$ complexes (Lewis acid sites).

3.2. TEMPERATURE PROGRAMMED DESORPTION OF AMMONIA

TPDA profiles for the two zeolite samples, namely [Al]-HZSM-5 and [Ga]-HZSM-5, are shown in fig. 1. The peak maxima in the NH_3 evolution profiles are observed at ca. 670 and 650 K, respectively, for the Al- and Ga-forms. This result is in good agreement with literature data [16] and represents the known sequence of the acid strength of these materials [15–18], namely [Al]-HZSM-5 > [Ga]-HZSM-5. The quantitative determination from the desorption peak areas of the desorbed amount of NH_3 and, hence, of the number of acid centers, shows that this value is similar for the alumino- and gallosilicate, consistent with the results of the chemical analysis and the inference that the Al^{3+} ions are quantitatively and the Ga^{3+} almost quantitatively incorporated within the zeolite framework. The calculated n_{Si}/n_{Al} and n_{Si}/n_{Ga} ratios are 23.8 and 29.5, respectively, suggesting that in fact some gallium is present in extra-lattice positions as also indicated by the NMR-results. In conclusion, the densities of Brønsted sites in the alumino- and gallosilicate are close although not identical.

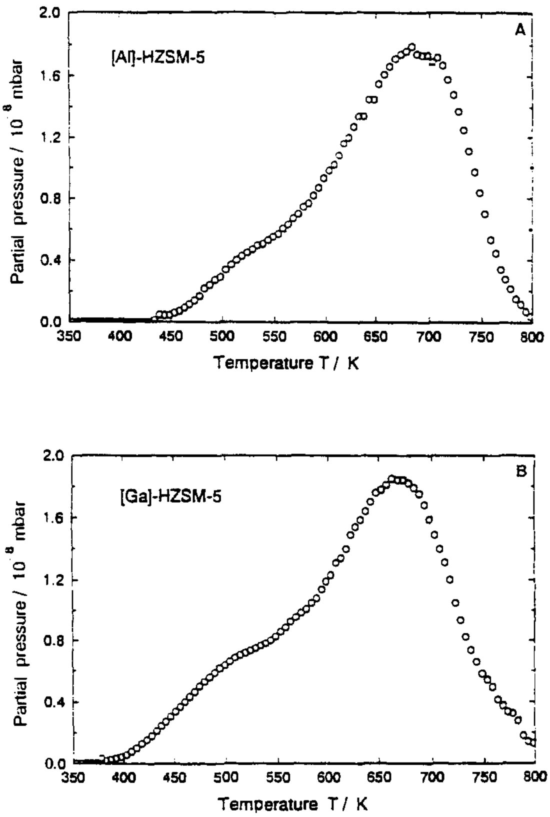

Fig. 1. Temperature programmed desorption spectra of ammonia from (A) [Al]-HZSM-5 and (B) [Ga]-HZSM-5.

3.3. HYDROXYL STRETCHING VIBRATIONS

The infrared spectra in the hydroxyl stretching regime between 3900 and 3200 cm^{-1} of the two zeolite samples are compared in fig. 2. The spectra were recorded at 77 K after thermal treatment at 673 K and evacuation. The principal band observed for [Al]-HZSM-5 is located at 3618 cm^{-1} with a band half width of 36 cm^{-1} (spectrum A in fig. 2) and is assigned as the O–H stretching mode of the acidic bridging framework OH groups of the type Si(OH)Al as frequently reported in the literature [8,9,12]. In addition, a relatively weak band at 3746 cm^{-1} with a shoulder at 3728 cm^{-1} is observed, which is attributed to isolated silanol groups located on the external surface of the zeolite [8,12] and to terminal OH groups of chains of H-bonded silanol groups [12], respectively. Pelmenschikov et al. [20] have attributed the band at 3720–3740 cm^{-1} to a bridging OH group with an exceptionally small SiOAl bond angle.

Bands characteristic of extra-framework Al_2O_3 are hardly detectable in the present sample, consistent with the structure characterization and TPDA results. It

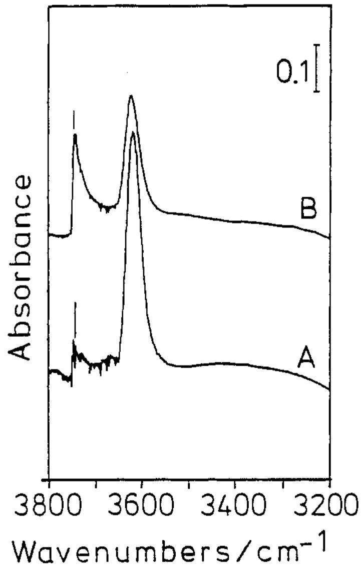

Fig. 2. Hydroxyl stretching infrared spectra after standard pretreatment of (A) [Al]-HZSM-5; (B) [Ga]-HZSM-5.

should be mentioned, that Zecchina et al. [12] have detected a comparably intense band at 3670 cm^{-1} which they ascribed to a "partially extra-framework species", its acid strength being lower than that of the predominant bridging OH groups but higher than that of the hydroxyl groups of extra-lattice Al_2O_3.

The principal band of [Ga]-HZSM-5 is slightly asymmetric and is located at 3622 cm^{-1} with a band half width of 36 cm^{-1} (spectrum B in fig. 2). This band is to be assigned as the O–H stretching mode of a bridging hydroxyl: Si(OH)Ga. The intensity of this band is lower than that of [Al]-ZSM-5 (spectrum A in fig. 2). This is probably due to the somewhat lower Ga^{3+} incorporation into the lattice and it may also be caused by a lower sample density in the infrared beam. A relatively strong band at 3747 cm^{-1} of isolated SiOH groups is observed. This band is asymmetric toward lower frequencies but resolved additional bands are not obvious. In particular, bands that might be associated with OH groups located on extra-lattice Ga_2O_3 cannot be detected.

The band positions at 3618 and 3622 cm^{-1} of the acidic framework OH groups of the type Si(OH)Me of [Al]-HZSM-5 and [Ga]-HZSM-5, respectively, are in fairly good agreement with literature data (see table 1) and follow the reported trends [16,17]. The increase of the O–H stretching frequencies in this series may well be attributed to the decreasing electron-withdrawing power in the sequence $Al^{3+} > Ga^{3+}$, and it has therefore been related to the decreasing acid strength with increasing frequency of the isolated unperturbed OH groups [16,17]. The correlation between O–H stretching frequency and acid strength is not unambiguous, although it seems to hold for hydroxyls being bonded in identical structures [21].

Table 1
Hydroxyl stretching frequencies of framework OH groups of zeolites and CO-induced frequency shifts $\Delta\nu_{OH}$

Zeolite	$n_{Si}/n_{Me^{3+}}$ (lattice)	ν_{OH} (cm^{-1})	$\Delta\nu_{OH}$ (cm^{-1})	Ref.
[Al]-HZSM-5	23.8	3618	313	present
	35	3610	–	16
	65	3610	–	17
	24	3617	312	8
	13.6	3617	312	9
	14–20	3625–3610	335–350	12
[Ga]-HZSM-5	29.5	3622	282	present
	99	3620	–	16
	34	3615	–	17
$H_{95}Na_5Y$	2.90	3643	296	9
$H_{90}Na_{10}Y$	2.47	3640	285	10
$H_{70}Na_{30}Y$	2.50	3647	278	9
$H_{40}Na_{60}Y$	2.50	3648	271	9
$H_{20}Na_{80}Y$	2.50	3650	265	9

The O–H stretching frequencies observed in the present study are consistently somewhat higher (up to 8 cm^{-1}) than those reported by Chu and Chang [16] and by Post et al. [17] as can be seen in table 1. It is inferred that this is due to the lower $n_{Si}/n_{Me^{3+}}$ framework ratios of the present samples. First experiments using [Al]-HZSM-5 zeolites with different aluminium contents seem to indicate in fact a decrease of the stretching frequency of framework OH groups with increasing n_{Si}/n_{Al} ratio. Furthermore, based on quantum chemical calculations, Kramer et al. [22] and van Santen et al. [23] have reported a decrease of the O–H stretching frequency of the high-frequency (HF) framework OH groups with increasing n_{Si}/n_{Al} ratio for HY-zeolites.

In addition to the absolute position of the O–H stretching frequencies of OH groups bonded in identical structures, the frequency shift that O–H vibrations experience on H-bonding to a given H-bond acceptor molecule (such as e.g. CO), can safely be regarded as a measure of the relative strength of the H-bonds, and this quantity should be directly related to the relative acid strength of the OH groups involved [1,2].

3.4. CARBON MONOXIDE ADSORPTION

Fig. 3 shows the infrared spectra in the O–H stretching region when CO is adsorbed on [Al]-HZSM-5 at 77 K in the pressure range up to 250 mbar, and fig. 4 shows the evolution of the corresponding spectra in the C–O stretching region. Clearly, in the low pressure range (0.3–1.0 mbar) only the bridging hydroxyls (band at 3618 cm^{-1}) are affected and a new broad band is growing in at 3305 cm^{-1} corre-

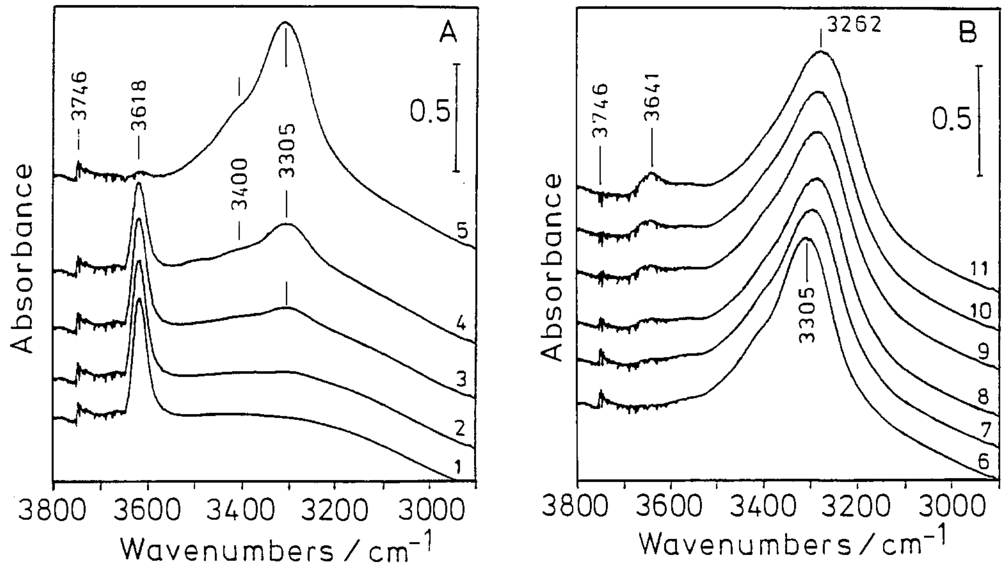

Fig. 3. Hydroxyl stretching infrared spectra of [Al]-HZSM-5 after CO adsorption at 77 K and pressures of (A) zero (1); 0.2 (2); 0.3 (3); 0.5 (4); 1.0 (5) mbar, and (B) 2.5 (6); 5.0 (7); 10.0 (8); 25.0 (9); 50.0 (10); 250 (11) mbar.

sponding to a shift $\Delta\nu_{OH} = 313$ cm^{-1} (fig. 3A). This band is accompanied by a shoulder at approximately 3400 cm^{-1}. The corresponding species is saturated at an equilibrium CO pressure of ca. 1 mbar when the band at 3618 cm^{-1} has entirely van-

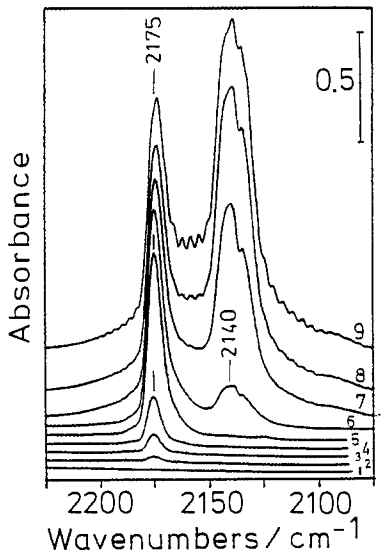

Fig. 4. Carbonyl stretching infrared spectra of [Al]-HZSM-5 after CO adsorption at 77 K and pressures of zero (1); 0.2 (2); 0.3 (3); 0.5 (4); 1.0 (5); 2.5 (6); 5.0 (7); 10.0 (8); and 25.0 (9) mbar.

ished and the shifted band has reached its maximum absorbance. Simultaneously an almost symmetric carbonyl band grows in at constant frequency of 2175 cm^{-1} with no additional band being detected in the C–O stretching region (spectra 1–5 in fig. 4). The appearance of these spectra is very close to spectra reported in the literature [8,12]. All the observed features except for the shoulder at 3400 cm^{-1} are characteristic of H-bonding of CO to the bridging hydroxyl Si(OH)Al and formation of a 1 : 1 OH···CO complex. In view of the fact, that H-bonding of CO onto isolated silanol groups on SiO_2 leads to a shift of the O–H stretching band of only ca. 90 cm^{-1} [6,7], the observed shift of 313 cm^{-1} is indicative of the high acid strength of the bridging OH groups. Consistent with the largely different acid strengths of the isolated silanols on the external surface and the bridging framework hydroxyls is the observation, that the O–H band of the former at 3746 cm^{-1} remains entirely unperturbed. These spectral effects are completely reversible on evacuation at 77 K or on temperature increase at constant CO pressure.

The appearance of the shoulder at ca. 3400 cm^{-1} is intriguing. It is reproducibly formed and has also been reported by others [8,12]. Zecchina et al. [12] have attributed this band to an H-bonded complex with CO of the so-called "partially extra-framework species" (unperturbed O–H stretching frequency at 3670 cm^{-1}). In the present study, however, a band at 3670 cm^{-1} of unperturbed OH groups was not detected (vide supra). Hence, an alternative interpretation of the shoulder at 3400 cm^{-1} is required. It has been shown earlier for amorphous silica–alumina [3] that CO adsorption produced several features in the band of perturbed OH groups suggesting H-bonded species having variable H-bond energies, although only one relatively sharp O–H stretching band of unperturbed OH groups was detected. Theoretical calculations had suggested that differences in SiOAl bond angles of bridging OH groups might affect the O–H stretching frequency [24] and hence, the H-bond donor strength. The observed width at half maximum of 36 cm^{-1} of the O–H stretching band of the framework hydroxyls is supposed to allow for a distribution of O–H force constants which might be due to small variations in local geometry. We thus infer that the observed shoulder at 3400 cm^{-1} and the asymmetry toward higher frequency of the principal band at 3305 cm^{-1} of associated OH groups might indicate some intrinsic heterogeneity of framework OH groups. The strong asymmetry of the TPDA-profile shown in fig. 1A is presumably also an indication of an acidity heterogeneity, which has been demonstrated to exist in several zeolite materials [25–27]. The most straightforward rationalization of this heterogeneity is an inhomogeneous distribution of Al^{3+} ions in the framework, so that locally n_{Si}/n_{Al} ratios lower than the average value of 24 can occur and lead to slight lattice distortions and, hence, variations in TOT bond angles (vide supra). Moreover, van Santen et al. [23] have demonstrated that local structure relaxation does occur on protonation/deprotonation. These authors have also concluded [23] from quantum chemical considerations, that addition of a second proton to a cluster consisting of four tetrahedra with two Al and two Si atoms weakens the O–H bond of the first hydroxyl and thus enhances its intrinsic acidity. One might thus also infer an adsorbate-induced modification of the acid strength provided more than one Al atom became bonded in a comparable structure unit. This may result in a response of the OH bond length of one hydroxyl group when the second becomes engaged in H-bonding. The extent of this effect, however, is not known.

Fig. 3B shows the development of the bands in the hydroxyl stretching region at increasing CO pressures (higher than 1.0 mbar) after the band at 3618 cm^{-1} of the framework OH groups has been completely eroded and the 1 : 1 OH···CO complex (band at 3305 cm^{-1}) has reached saturation. As the CO pressure exceeds 2.5 mbar, the principal band at 3305 cm^{-1} broadens and the maximum shifts to lower frequency. A value of 3262 cm^{-1} is reached at an equilibrium CO pressure of 250 mbar. Simultaneously, a new band at 2140 cm^{-1} develops in the carbonyl stretching region (see spectra 6–10 in fig. 4), which is assigned to physically adsorbed CO [3,4,7,10,12]. Similar shifts of the O–H stretching band of H-bonded silanol groups on SiO_2 have also been reported by Beebe et al. [7] when physically adsorbed CO was present. These authors explained the shift as being due to a solvent effect brought about by a liquid-like CO phase. Echoufi and Gélin [10] have observed the same phenomena when CO was adsorbed on decationated Y-type zeolites. It is thus important to determine $\Delta\nu_{OH}$ values free of any such solvent effects when the O–H frequency shift is to be used as a measure of relative acid strengths.

The tailing that becomes evident in the carbonyl spectra of fig. 4 at high and low frequencies when the pressure is equal to or higher than 5 mbar are interpreted as rotational wings to the 2140 cm^{-1} band [7,10]. Physically adsorbed CO in the ZSM-5 channels should thus exhibit some rotational freedom.

It can also be seen in fig. 3B that the band at 3746 cm^{-1} of SiOH groups at the external surface becomes progressively perturbed as the CO pressure increases and a new band develops in concert at 3641 cm^{-1}. This position corresponds to a frequency shift of 107 cm^{-1} suggesting the formation of SiO–H···CO species, which is confirmed by the increasing absorbance at approximately 2160 cm^{-1} in the carbonyl spectra of fig. 4. A band at 2158 cm^{-1} has been reported for CO being H-bonded to isolated SiOH groups on SiO_2 [7].

The spectral effects of CO adsorption on [Ga]-HZSM-5 are shown in figs. 5 and 6. The development of the hydroxyl stretching spectra (fig. 5) very much resembles that observed for [Al]-HZSM-5. At low coverages the framework OH groups (band at 3622 cm^{-1}) are the first to be perturbed and a broad band of H-bonded species develops at 3340 cm^{-1} together with a shoulder at approximately 3440 cm^{-1}. Simultaneously, a band of H-bonded CO grows at 2172 cm^{-1} in the carbonyl stretching spectra (spectra 1–5 in fig. 6). This band reaches maximum absorbance at about 1.0 mbar equilibrium CO pressure, when the O–H stretching band of unperturbed framework OH groups is fully eroded (spectra 5 in figs. 5 and 6). This observation is consistent with a 1 : 1 H-bonded complex between CO and Si(OH)Ga framework hydroxyls. The frequency shift $\Delta\nu_{OH}$ at saturation coverage amounts to 282 cm^{-1}, and is thus significantly smaller than that observed for the aluminosilicate. At higher CO pressures and hence coverages,

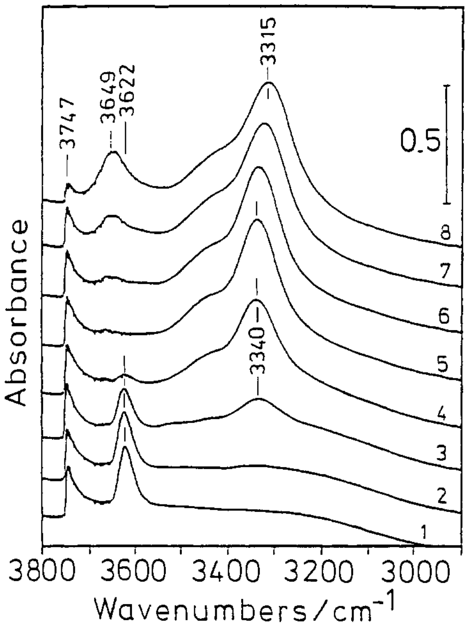

Fig. 5. Hydroxyl stretching infrared spectra of [Ga]-HZSM-5 after CO adsorption at 77 K and pressures of zero (1); 0.1 (2); 0.2 (3); 0.5 (4); 1.0 (5); 2.5 (6); 5.0 (7) and 10.0 (8) mbar.

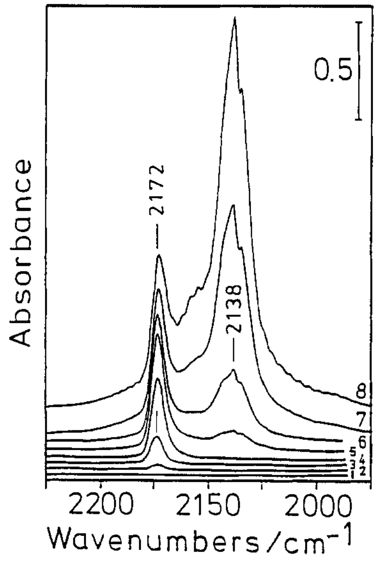

Fig. 6. Carbonyl stretching infrared spectra of [Ga]-HZSM-5 after CO adsorption at 77 K and pressures of zero (1); 0.1 (2); 0.2 (3); 0.5 (4); 1.0 (5); 2.5 (6); 5.0 (7) and 10.0 (8) mbar.

physical adsorption occurs as evidenced by the development of the carbonyl band at 2138 cm^{-1} (spectra 5–8 in fig. 6) and the band of associated framework OH groups consequently shifts from 3340 to 3315 cm^{-1} due to solvent effects. The assignment of the shoulder at 3440 cm^{-1} to intrinsic heterogeneity of framework OH groups follows the arguments given above for the aluminosilicate. Starting at about 1 mbar CO the SiOH groups at the external surface are perturbed by H-bonding to CO as indicated by the decreasing absorbance of the band at 3747 cm^{-1} and the simultaneous evolution of a shifted band at 3649 cm^{-1} ($\Delta\nu_{OH} = 98$ cm^{-1}) and of the characteristic band at 2155 cm^{-1} in the carbonyl region (fig. 6).

3.5. RELATIVE ACID STRENGTHS AND COMPARISON WITH LITERATURE DATA

Hydroxyl stretching frequencies of framework OH groups and frequency shifts induced by CO adsorption as observed for the [Al]- and [Ga]-HZSM-5 samples in the present study are compared with data reported in the literature in table 1. The band positions of the unperturbed O–H groups of the two ZSM-5 type zeolites coincide fairly well with those reported in the literature if the different compositions are taken into account. In particular, the trend in band position [Al] < [Ga] reflects the opposite trend in acid strength.

Comparing the frequency shifts $\Delta\nu_{OH}$ observed for [Al]-HZSM-5 samples by various research groups, a surprisingly good agreement is found (see table 1), the $\Delta\nu_{OH}$-value being 310–315 cm^{-1}. Only the data of Zecchina et al. [12] deviate significantly for unknown reasons. Consistent with the lower acid strength of [Ga]-HZSM-5, the CO-induced frequency shift is only 282 cm^{-1}. This value falls within the range of frequency shifts that were reported for HNaY zeolites as listed in table 1. It may thus be inferred that the gallosilicate has an acid strength comparable to that of HNaY-zeolites at high degrees of exchange.

The trends in ν_{OH} and $\Delta\nu_{OH}$ in the series of $H_xNa_{100-x}Y$-zeolites listed in table 1 are of interest. All samples listed have nearly the same n_{Si}/n_{Al} ratio. As the degree of exchange increases, the O–H stretching frequency of the high-frequency (HF) hydroxyls decreases suggesting increasing acid strength with increasing proton concentration. This is also reflected in the frequency shifts produced on CO adsorption which increase as the stretching frequency decreases. These observations nicely coincide with the theoretical predictions of van Santen et al. [23], which (as discussed above) has shown that increased proton concentration may enhance the intrinsic acid strength of zeolite materials.

4. Conclusions

A systematic study of the use of CO as a probe of protonic acidity of HZSM-5 type zeolites was carried out. The frequency shift of the O–H stretching mode of acidic Si(OH)Me hydroxyl groups induced by H-bonding of CO at 77 K is considered to be a measure of the H-bond donor strength and of the acid strength of the OH group. The IR-band of associated OH groups on [Al]-HZSM-5 was found to be shifted to lower frequency relative to the band of unperturbed acidic OH groups by 313 cm^{-1}, this being a measure of the H-bond strength. The band is asymmetric toward higher frequencies and has a shoulder near 3400 cm^{-1}. It is suggested that this is due to an intrinsic heterogeneity of acidic hydroxyl groups which may be due to slight variations in the local geometries possibly imposed by an inhomogeneous distribution of Al^{3+} ions in the framework.

When [Ga]-HZSM-5 with slightly lower acid site density than that of [Al]-HZSM-5 was used, a smaller OH stretching frequency shift of 282 cm^{-1} was found consistent with the lower acid strength of the gallium silicate. Interestingly, this frequency shift falls into the range of frequency shifts that have been reported for HNaY zeolites suggesting similar acid strengths for these two types of zeolite materials.

CO is recommended as a sensitive probe of zeolite acid strength in combination with IR-spectroscopy. The OH stretching frequency shift induced by H-bonding of a CO molecule with an O–H oscillator is a measure of the relative acid strength of different zeolite materials, provided the experimental frequencies are free of any perturbations by solvent effects and cationic extra-framework species. The former may become influential with increasing CO equilibrium pressures, when liquid-like CO is present in the zeolitic pore system.

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