Ferrierite and SUZ-4 Zeolite: Characterization of Acid Sites

Vladimir L. Zholobenko,*,† Dmitri B. Lukyanov, and John Dwyer*

Chemistry Department, Centre for Microporous Materials, UMIST, P.O. Box 88, Manchester, M60 1QD, U.K.

Warren J. Smith

BP Chemicals, Research and Engineering, Sunbury on Thames, U.K.

Received: October 15, 1997; In Final Form: January 22, 1998

A detailed FTIR characterization of acid sites in two structurally related zeolites, ferrierite and SUZ-4, is carried out. Assignment of OH groups observed in the spectra is addressed taking into account zeolite structure and composition. In ferrierite, at least four types of bridging OH groups vibrating in 10-, 8-, and 6-membered rings are identified using a combination of experimental and computational techniques. Our results suggest that framework aluminum in ferrierite is preferentially sited in extended rings at the intersections of 8- and 6-ring channels resulting in a high concentration of OH groups in the large cages in 8-ring channels. The IR band corresponding to these hydroxyls, 3601 cm^{-1}, is not significantly shifted to low frequencies because the OH groups are vibrating in extended rings. At the same time, access to these hydroxyls is restricted by 8-membered rings. The band at 3565 cm^{-1} assigned to the bridging OH-groups in 6-membered rings is responsible for the strongly asymmetric shape of the experimental spectrum. For SUZ-4 zeolite, deconstruction of the spectrum, supported by H–D exchange and accessibility studies, results in three IR bands at 3560, 3592, and 3610 cm^{-1} corresponding to OH groups in 6-, 8- and 10-membered rings. The intensity of the first band is considerably lower than that in ferrierite, indicating that the residual potassium cations are located in small cages or in double 6-rings. The low-intensity band at 3560 cm^{-1} and the similar intensities of the bands at 3592 and 3610 cm^{-1} lead to a near-symmetrical experimental spectrum.

Introduction

Over the past few decades much research has been focused on synthesis, characterization, and catalysis on zeolites.[1–3] Only few of these materials, however, are used commercially as ion-exchange builders, adsorbents, or catalysts. There is consequently a significant incentive (i) to utilize known zeolites in novel applications and (ii) to produce new materials with potentially useful properties. In this context, the ferrierite family of zeolites, described by R. Gramlish-Meier,[4] provides an important example. Although they are known catalysts,[5,6] siliceous ferrierite type materials have been utilized commercially as a highly selective catalyst for linear butene isomerization[7,8] only recently. Within the past 5 years, two new zeolites closely related to ferrierite, SUZ-4[9] and ZSM-57,[10] have been synthesized by researchers from BP and Mobil, respectively. Their structures have also been reported.[10,11] Comparative characterization of molecular sieves from this group can provide key information for the design of the optimum catalysts for selective transformation of olefins.

IR spectroscopy is recognized as a powerful means for the investigation of acid sites in zeolitic materials.[12–14] For instance, characterization of OH groups in multichannel zeolite frameworks has attracted significant attention.[12,15,16] In faujasite and related materials, two infrared bands originating from OH groups located in large and small cages (high-frequency and low-frequency bands, respectively) are well documented.[1,12,15] In recent FTIR studies,[16–18] the hydroxyl region of the infrared spectrum of mordenite has been reexamined using adsorption of test molecules, and strong evidence for the presence of two types of bridging OH groups in 12- and 8-membered channels of mordenite has been provided. In this work we extend the same approach to the investigation of acid sites in SUZ-4 zeolite and ferrierite. Both zeolites feature 10-, 8-, 6-, and 5-membered rings in their structure.[11,19] Therefore, deconstruction of the hydroxyl region requires careful application of experimental and computational techniques, since the presence of several OH bands can be expected in the IR spectra.[15] In this paper we present detailed characterization of acid sites in SUZ-4 zeolite in comparison with ferrierite in order to facilitate optimization of their catalytic performance.

Experimental Section

Materials. The detailed synthesis procedure for SUZ-4 zeolite is given in refs 9 and 20. A sample of ferrierite was provided by BP Chemicals. Chemical composition of the calcined materials was $K_{4.6}Na_{0.4}Al_{5.0}Si_{31.0}O_{72}$ (Si/Al = 6.2) for SUZ-4 zeolite and $K_{4.3}Na_{0.6}Al_{4.9}Si_{31.1}O_{72}$ (Si/Al = 6.3) for ferrierite. Zeolites were twice ion-exchanged with NH_4NO_3 solution at 60 °C. O_2 (99.9%), D_2 (99.7%), ethane (99.95%), *n*-butane (99.5%), and isobutane (99.5%) were obtained from Messer Griesheim. Py (99+%) and NH_3 (99.999%) were supplied by Aldrich Chemical Co. and *n*-hexane (99.5%) by Fluka.

XRD. XRD analysis of as-made powdered samples was carried out using a Philips 1710 diffractometer scanning at 1°/min (2θ range from 5 to 40°).

NMR. ^{27}Al and ^{29}Si MAS NMR spectra of the hydrated samples were obtained at room temperature employing a Bruker MSL 400 NMR spectrometer. $Al(NO_3)_3$ and TMS were used as references.

† New address as of April 1, 1998: Chemistry Department, Keele University, Keele, Staffordshire ST5 5BG, U.K. E-mail: v.zholobenko@ keele.ac.uk. Fax: 44 (0) 1782-712378.

FTIR. IR spectra of self-supported zeolite disks were collected at a resolution of 2 cm^{-1} using a Nicolet Magna 550 FTIR spectrometer. To exclude possible artifacts associated with traces of water present, zeolite samples were H–D-exchanged with D$_2$ (partial pressure of 50 Torr) at 200–400 °C. Effective acidity of the catalysts was assessed using thermodesorption of ammonia monitored by the spectrometer. Py was used as a probe molecule to characterize Lewis and Brønsted acid sites. Adsorption of C$_2$–C$_6$ alkanes was carried out to study accessibility and acidic properties of OH groups. The detailed experimental procedure was described recently.[16,21] OMNIC 2.1 (Nicolet Instruments Corp.) and Microcal Origin 3.54 (Microcal Software Inc.) software packages were used for spectral data analysis.

Results and Discussion

NMR, XRD, and Chemical Analysis. XRD characterization of as-synthesized molecular sieves indicates high crystallinity of the samples. The diffraction patterns agree with those reported in the literature for ferrierite and SUZ-4.[9,11,22] Si/Al ratios obtained from chemical analysis for both zeolites have very similar values (6.2–6.3). It should be noted that ~25% of potassium counterions is left in the SUZ-4 sample. According to S. L. Lawton et al.,[11] these cations are trapped in the small cages of the SUZ-4 structure. ^{27}Al NMR spectra of both zeolites show the only peak at 56 ppm attributed to tetrahedral framework Al,[23,24] reflecting retention of aluminum in the framework. Only traces of Lewis acid sites are detected in calcined and ion-exchanged materials using FTIR-monitored adsorption of Py. More details of characterization are given in ref 20.

FTIR Studies. The OH and OD regions of the IR spectra for H and D forms of ferrierite and SUZ-4 zeolite are presented in Figures 1 and 2. In agreement with previous reports,[8,25,26] an intense band of bridging hydroxyls and a weak silanol band in ferrierite are observed at 3602 and 3746 cm^{-1}, respectively. In the H–D-exchanged sample the corresponding OD bands appear at 2658 and 2761 cm^{-1} (see Table 1). Close examination reveals that hydroxyl IR bands are asymmetric, which is particularly evident from the first derivative of the spectrum. The asymmetry of the SiOH (SiOD) band can be attributed to the presence of terminal SiOH in the zeolite and in the traces of amorphous silica in the sample and also to the hydrogen bonding of silanols.[27,28] Frequencies of Si(OH)Al group vibrations in zeolites depend generally on local structure and composition. In agreement with previous reports,[29,30] our ^{29}Si NMR data demonstrate the presence of both Si(1Al) and Si(2Al) sites. Also, Si(OH)Al groups can vibrate in 10-, 8-, 6-, or 5-membered rings, giving rise to a number of OH bands in the IR spectrum.[12,15,16,31] Consequently, there can be several types of bridging OH groups contributing to the asymmetric band at 3602 cm^{-1}.

The IR spectra of SUZ-4 zeolite also contain SiOH and Si-(OH)Al groups or their D analogues (see Figure 2 and Table 1). The silanol band is asymmetric as in ferrierite. The band of bridging hydroxyls, however, shows practically no asymmetry in the spectrum and in its first derivative. It should be noted that the maximum achieved degree of ion exchange in SUZ-4 is ~75% with the residual potassium cations located in small cages[11] or perhaps in the double 6-rings (D6R). Consequently, bridging OH groups in the studied H,K–SUZ-4 sample should be located mainly in 8- and 10-membered rings. Although both Si(1Al) and Si(2Al) sites are detected using ^{29}Si NMR, there is no IR spectroscopic evidence for the presence of two different
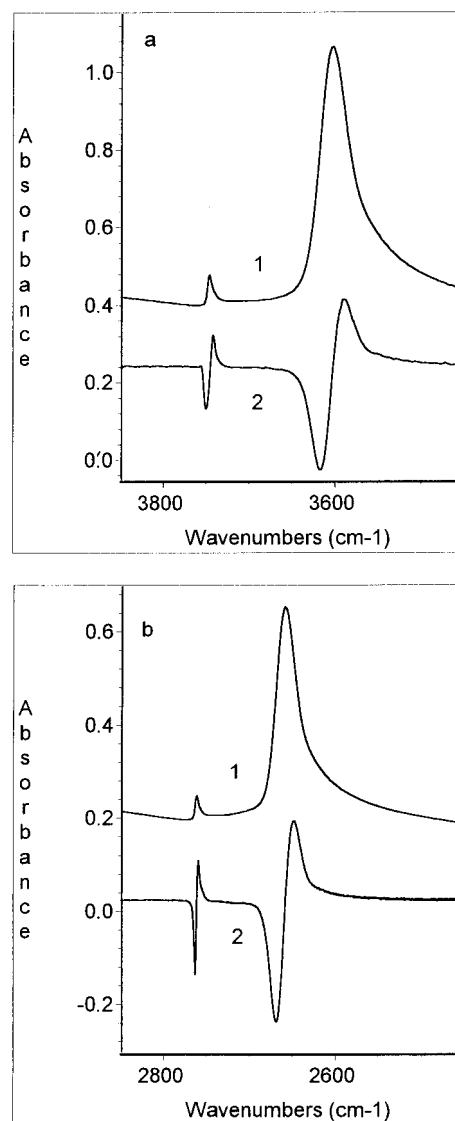

Figure 1. OH and OD regions of (1) the IR spectra of ferrierite and (2) their first derivatives: (a) H form; (b) D form.

acidic OH (OD) groups related to these sites. Comparing NMR and FTIR results for ferrierite and SUZ-4 zeolites, we can suggest that the asymmetry of IR bands at 3602 (2658) cm^{-1} in ferrierite is not due to two types of bridging OH (OD) groups associated with differences in local composition and features related to Si(1Al) and Si(2Al) sites in the same channels but should be attributed to Si(OH)Al moieties vibrating in channels or cages of different size.

The accessibility and acidic properties of bridging hydroxyls in zeolites can be probed using a number of test molecules such as NH$_3$, Py, CO, and many others.[12–14] Ammonia temperature-programmed desorption (TPD) curves obtained from IR data for H–ferrierite, H,K–SUZ-4, and H–ZSM-5 (Si/Al = 17) are shown in Figure 3. It should be stressed that TPD data reflect the effective acidity, which depends on the "intrinsic" acidity, the acid-site density, size and structure of the pores, and crystal size.[16,32] The results obtained indicate higher apparent acidity of ferrierite. However, the presence of substantial amounts of K$^+$ in SUZ-4 is expected to result in a reduction of acid strength. Ammonia, having a kinetic diameter of $\sigma = 2.6$ Å, interacts, at 150 °C, with all bridging hydroxyls in H–ferrierite, H,K–SUZ-4, and H–ZSM-5, resulting in a gradual decrease in intensity of the Si(OH)Al band (see for example Figure 4a). For all three
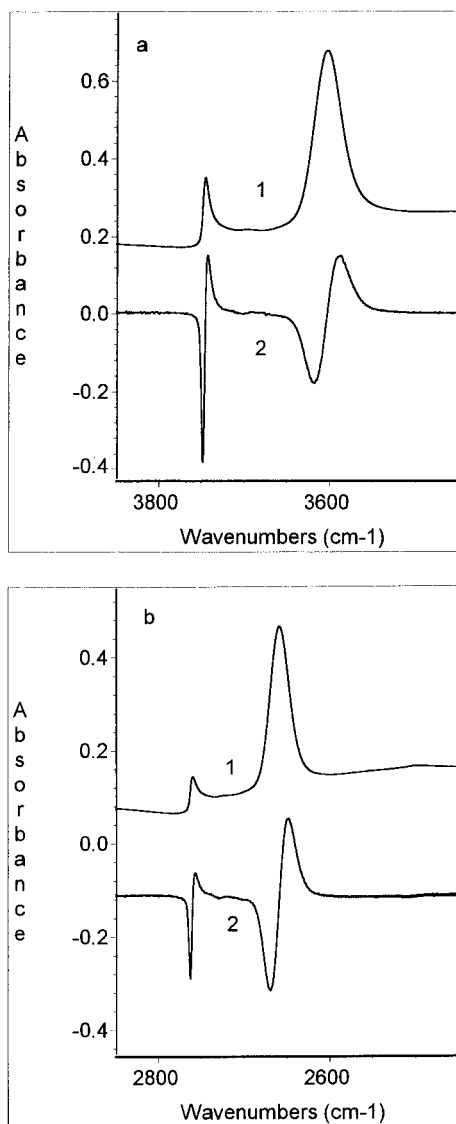
Ferrierite and SUZ-4 Zeolite

J. Phys. Chem. B, Vol. 102, No. 15, 1998 **2717**

Figure 2. OH and OD regions of the IR spectra of SUZ-4 zeolite (1) and their first derivatives (2): (a) H form; (b) D form.

TABLE 1: Spectral Parameters of Hydroxy Groups in Ferrierite, SUZ-4, and ZSM-5 Zeolites (cm^{-1})

sample (Si/Al ratio)	Si(OH)Al		SiOH		Si(OD)Al		SiOD	
	ν	HW[a]	ν	HW[a]	ν	HW[a]	ν	HW[a]
ferrierite (Si/Al = 6.3)	3602	44	3746	8	2658	31	2761	6
SUZ-4 (Si/Al = 6.2)	3603	38	3746	11	2659	26	2760	9
ZSM-5 (Si/Al = 17)	3610	29	3744	10				

[a] Peak width at half-height.

zeolites, the peak position and shape of the band do not change, demonstrating no preferential adsorption of ammonia (strong base) on bridging OH groups (strong acid sites). Subsequent TPD experiments could be used to discriminate bridging OH groups located in various pores, since they should possess different effective acidity.[16] However, only minor changes in the position of the OH band, such as a shift from 3607 to 3603 cm^{-1}, in the IR spectra of ferrierite are observed during desorption of ammonia. These minor changes can be explained by subtle inhomogeneity of acid sites due to differences in their geometry, chemical environment, and location. This result also
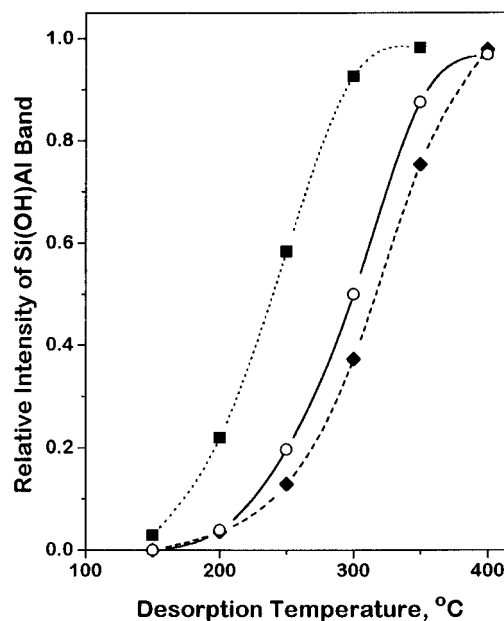

Figure 3. Ammonia TPD curves obtained from IR data for ferrierite (◆), SUZ-4 (○), and ZSM-5 (■).

indicates that IR bands of Si(OH)Al groups vibrating in 8- and 10-ring channels have very similar peak positions.

Upon ammonia thermodesorption from SUZ-4 zeolite at 150−250 °C, a relatively narrow band of Si(OH)Al groups is observed in the IR spectra at 3610 cm^{-1} (peak width at half-height, HW = 30 cm^{-1}), which can be considered as a high-frequency (HF) component of the original hydroxyl band at 3603 cm^{-1} (Figure 4b). At higher desorption temperatures the Si-(OH)Al band is gradually restored to its initial shape and intensity. Using IR spectra obtained during NH$_3$ adsorption and desorption, we can now reveal the low-frequency (LF) component of the hydroxyl band. The difference spectrum (Figure 5) clearly shows the LF peak, with the maximum at 3593 cm^{-1} and HW = 33 cm^{-1}, corresponding to the fraction of OH groups retaining ammonia at 250 °C. The stronger interaction of LF hydroxyls with ammonia can be accounted for by the multipoint interaction of NH$_4^+$ cations with oxygen atoms in smaller pores or by enhanced acidity of these hydroxyls. It should be noted that in a very similar experiment, LF and HF OH bands have been previously detected in IR spectra of mordenite.[16]

The LF hydroxyl IR bands are frequently assigned to OH groups vibrating in small cages.[12,15,16] Indeed, accessibility studies on SUZ-4 zeolite demonstrate that upon isobutane adsorption the 3603 cm^{-1} band shifts toward lower wavenumbers and decreases in intensity (Figure 6). Isobutane, σ = 5.0 Å, can only interact with OH groups in 10-ring channels, which constitute therefore the HF component of the band at 3603 cm^{-1}. The remaining band at 3599 cm^{-1} represents the LF hydroxyls vibrating in 8-ring channels being inaccessible for isobutane. This confirms the difference in the location of the hydroxyls rather than in the chemical environment for HF and LF OH groups. However, the intense IR band of hydroxyls H-bonded to isobutane molecules, at ∼3528 cm^{-1}, prevents determination of the exact positions of the LF and HF hydroxyl bands from these experiments. The results of accessibility studies of bridging OH groups in ferrierite, SUZ-4, and ZSM-5 zeolites (described in detail in ref 20) are summarized in Table 2. It is worth noting that in ferrierite, relatively small *n*-hexane molecules (σ = 4.3 Å) interact with all hydroxyls in 10-membered rings but only with some of the OH groups located

Figure 5. OH region of the IR spectra of SUZ-4 zeolite obtained during (1) ammonia adsorption (spectrum 3 from Figure 4a) and (2) desorption (spectrum 2 from Figure 4b) and (3) their difference.
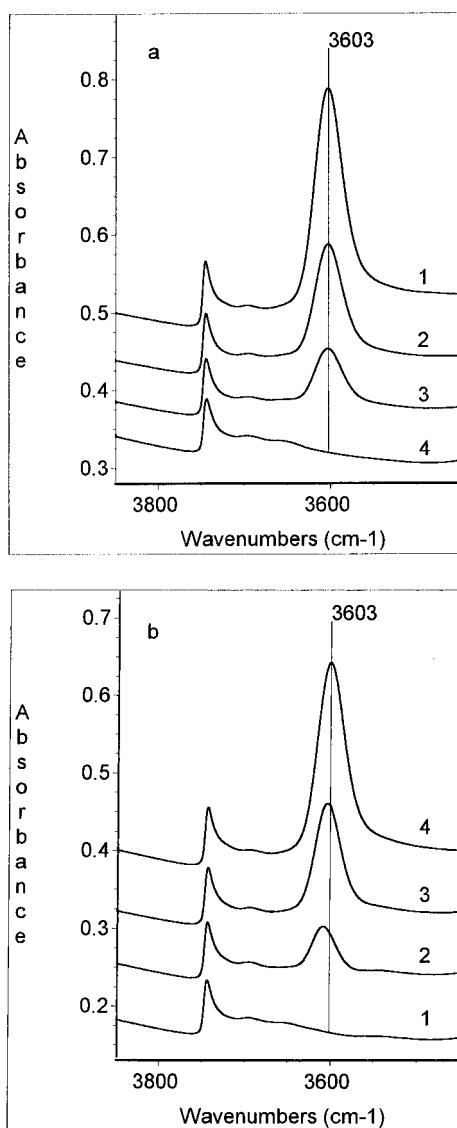

Figure 4. OH region of the IR spectra of SUZ-4 zeolite: (a) ammonia adsorption, (1) initial, (2) 0.55 mmol/g, (3) 0.84 mmol/g, (4) 1.34 mmol/g; (b) ammonia desorption at (1) 150, (2) 250, (3) 300, and (4) 350 °C.

Figure 6. IR spectra of SUZ-4 zeolite before (1) and after isobutane adsorption at 2 Torr (2) and 130 Torr (3).

TABLE 2: Accessibility of Bridging OH Groups in Ferrierite, SUZ-4, and ZSM-5 Zeolites

sample	fraction of OH groups accessible to isobutane, %	fraction of OH groups accessible to n-hexane, %	OH band shift upon n-hexane adsorption, cm^{-1}
ferrierite	23	70	117
SUZ-4	44	97	122
ZSM-5	100	100	136

in 8-membered rings. This is qualitatively in agreement with theoretical calculations[33] and IR studies[26] demonstrating exclusion of long n-alkane molecules from 8-ring channels of ferrierite and could be attributed to a partial 8-ring pore blocking by the n-hexane molecules adsorbed in 10-ring channels. We can also conclude that the pore structure of SUZ-4 zeolite is more open compared with that of ferrierite.

The value of the bathochromic shift for the IR band of hydroxyls H-bonded to n-hexane molecules, used as a qualitative measure of acidity for bridging OH groups, gives the following order of acidic strength in zeolites: H−ZSM-5 > H−SUZ-4 ≥ H−ferrierite. This trend is different from that obtained using TPD, since ammonia thermodesorption reflects the effective acidity, which depends on a number of structural features and transport effects. By contrast, our IR measurements provide more direct information on the "intrinsic" acidity of bridging OH groups.

Our IR results have been used to test a number of models for deconstruction of the bridging OH band in the IR spectra of ferrierite. Curve fitting of the spectrum using only two peaks, as suggested previously in ref 25, does not give satisfactory
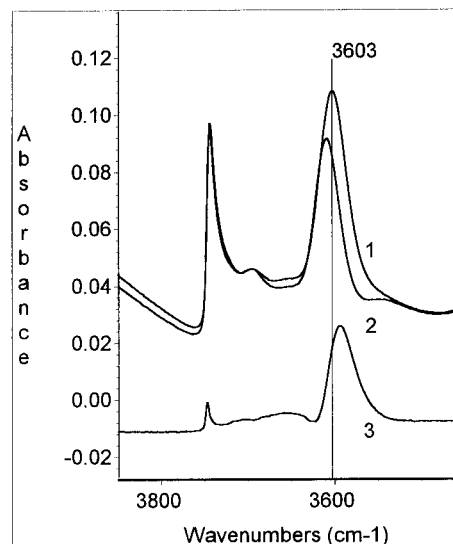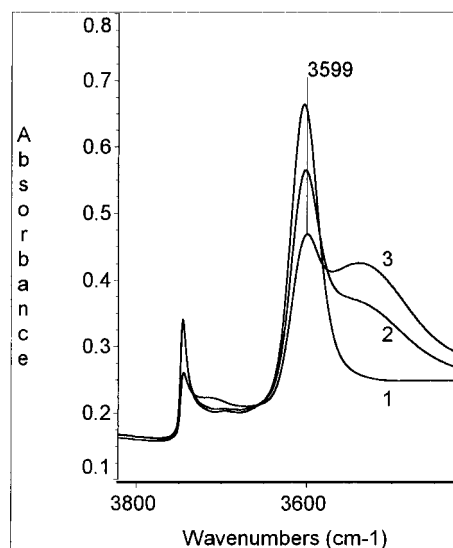
results. Although a good fit can be obtained by decomposition based on three peaks, their position, widths, and relative intensities do not compare well with experimental data obtained from ammonia TPD and accessibility studies. Modification of these three peaks to account for experimental results leads to a very poor curve fit. Our FTIR data indicate the presence of at least four components contributing to the bridging OH band (at about 3610, 3600, 3585, and 3550 cm^{-1}). Deconstruction of the OH region using these parameters generates a very good fit. However, an examination of the peak width predicted by

Ferrierite and SUZ-4 Zeolite

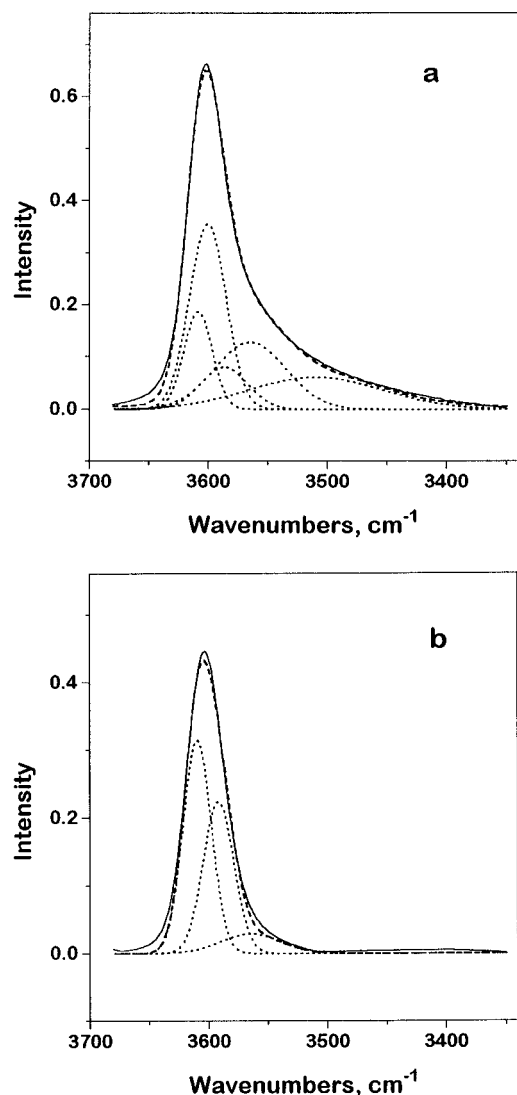*J. Phys. Chem. B, Vol. 102, No. 15, 1998* **2719**

Figure 7. Decomposition of the bridging OH band in the IR spectra of ferrierite (a) and SUZ-4 zeolite (b): —, experimental spectra; - - -, computed spectra; ···, single components.

TABLE 3: Calculated and Experimental Values of Bathochromic Shifts for OH Groups Vibrating in Zeolite Channels of Different Size

zeolite	ring type[a]	d_{min}[b] Å	calcd[b] $\Delta\nu_{OH}$ cm^{-1}	obsd[c] $\Delta\nu_{OH}$ cm^{-1}
ferrierite	10-membered	3.7	15	3
	extended ring	4.7	0	11
	8-membered	3.1	31	25
SUZ-4	10-membered	3.65	16	2
	8-membered	3.15	30	21
mordenite[d]	12-membered	4.6	1	0
	8-membered	3.2	28	27
	8-membered	2.65	52	

[a] Note the nonplanar shape of the rings. [b] See eq 1. d_{min} (Å) is the distance from the center to the nearest oxygen in a ring.[15] [c] 3612 cm^{-1} band found for OH groups vibrating in 12-ring channels of mordenite[16] is taken as the position ν_0 of an unperturbed bridging OH group. [d] Experimental data for mordenite are from ref 16.

accessible to both *n*-hexane and isobutane. The intense peak at 3601 cm^{-1} should be assigned to OH groups in large cages in 8-ring channels (∼50% of bridging OH groups). Indeed, this band is not significantly shifted, from vibration in 10-ring channels, to lower frequencies because the OH groups are vibrating in extended rings at the intersections of 8- and 6-ring channels, which are characterized by d_{min} = 4.7 Å (d_{min} is the distance from the center to the nearest oxygen in a ring;[15] see Table 3). At the same time, access to these hydroxyls is restricted by 8-membered rings, preventing adsorption of isobutane and bulkier molecules. Our results suggest that aluminum substitution in ferrierite preferentially occurs in extended rings at the intersections of 8- and 6-ring channels. The low-intensity band at 3587 cm^{-1} can be attributed to Si-(OH)Al groups in 8-membered rings. These hydroxyls should be accessible to *n*-hexane but not to isobutane. The position of this band should be shifted to lower wavenumbers owing to electrostatic interaction with the nearest oxygen atoms.[15] The band at 3565 cm^{-1} corresponds to bridging OH groups located in 6-membered rings, and it is responsible for the strongly asymmetric shape of the experimental spectrum.

Given the structure of SUZ-4 zeolite, one can expect the presence of three bands in the IR spectrum of the bridging hydroxyls corresponding to OH groups in 6-, 8-, and 10-membered rings. Deconstruction of the spectrum, supported by H–D exchange and accessibility studies, gives three IR bands at 3565, 3592, and 3610 cm^{-1} (Figure 7b). The intensity of the first band, assigned to OH groups in 6-membered rings, is considerably lower than the corresponding band in ferrierite indicating, in agreement with ref 11, that the residual potassium cations are concentrated in small cages or in double 6-rings. The intense band at 3610 cm^{-1} corresponds to Si(OH)Al groups in 10-membered rings, which are similar to 10-membered rings in ferrierite. These hydroxyls in 10-membered rings (∼50% of Si(OH)Al groups) are accessible to both *n*-hexane and isobutane. The peak at 3592 cm^{-1} (∼40% of bridging OH groups) can be assigned to OH groups in 8-ring channels. This band is expected to be shifted to lower frequencies because of electrostatic interaction with the nearest oxygen atoms (Table 3). These hydroxyls in 8-ring channels can interact with *n*-hexane but not with isobutane. We can conclude that the low-intensity band at 3565 cm^{-1} and the similar intensities of the bands at 3592 and 3610 cm^{-1} lead to the nearly symmetrical shape of the experimental spectrum.

In considering hydroxy groups observed in ferrierite and SUZ-4 zeolite, one should take into account differences in their structure, composition, and aluminum distribution. Indeed, in

decomposition reveals a band at 3550 cm^{-1} that is too broad, in disagreement with results of previous studies that indicate a linear correlation between the position of OH bands and their width.[21,34] Consequently, we suggest the presence of a fifth band. It is to be expected that an improved fit would follow with increasing number of peaks; however, for a proper deconstruction as opposed to a general curve fit there must be experimental evidence for peak selection. From this viewpoint we discuss below the results of experimentally supported deconstruction of the OH region in the FTIR spectra of ferrierite and SUZ-4 zeolite.

An excellent fit of the experimentally observed spectrum of H–ferrierite has been obtained using five peaks corresponding to OH groups vibrating in pores of different size (Figure 7a). The first four bands at 3609, 3601, 3587, and 3565 cm^{-1} should be assigned to bridging OH groups located in 10-ring channels, in large cages in 8-ring channels, and in 8- and 6-membered rings, respectively. The presence of the fifth band at 3510 cm^{-1}, which could be attributed to OH groups in 5-membered rings,[31] is not unambiguous, and satisfactory decomposition can be carried out using the four major bands. The 3609 cm^{-1} band can be attributed to Si(OH)Al groups in 10-membered rings. These hydroxyls, amounting to ∼20% of Si(OH)Al groups, are

2720 *J. Phys. Chem. B, Vol. 102, No. 15, 1998*

Zholobenko et al.

a fully ion-exchanged sample of ferrierite, acidic hydroxyls can be found in 6-, 8-, and 10-membered rings. In SUZ-4 zeolite, nonexchangeable potassium cations are probably located in small cages[11] or in the double 6-rings. Consequently, bridging OH groups in K,H−SUZ-4 are to be expected mainly in 8- and 10-membered rings. The problem of aluminum distribution in ferrierite has been addressed in a number of publications. The results obtained vary considerably, indicating the difficulty in calculating patterns of Al incorporation into zeolite frameworks. For instance, depending on the method chosen for calculations, some authors consider T2 and T4,[35,36] T1 and T2 [30] or T2, and T3 and T4 [37] sites to be most favorable for Al substitution, whereas others[29] assume random distribution of aluminum in ferrierite. To the best of our knowledge, no information is available on Al location in SUZ-4 zeolite. Clearly, more work is required in this area, which may provide key information for understanding the high selectivity of ferrierite-based catalysts in olefin transformations.

According to P. A. Jacobs and W. J. Mortier,[15] IR bands of bridging hydroxyls located in 6- and 8-membered rings undergo a bathochromic shift, $\Delta\nu$, given by

$$\Delta\nu = 24.32 - \frac{537.74}{d_{\min}^2} \qquad (1)$$

where $d_{\min}$ (Å) is the distance from the center to the nearest oxygen in a ring. This electrostatic model yields positions of OH bands in IR spectra for a range of zeolites by relating the $\Delta\nu$ value to the dimensions of a ring accommodating the OH group. This approach is proven to be useful for assigning OH bands in IR spectra to bridging hydroxyls vibrating in different structural elements of zeolites or, alternatively, to determine the location of Si(OH)Al groups from infrared spectra. However, our results demonstrate (Table 3) that calculated and experimental values of bathochromic shifts for OH groups can differ significantly for two reasons. First, it is difficult experimentally to resolve overlapping bands in the spectra of multichannel zeolites. Second, the simple electrostatic model[15] does not take into account the exact shape of nonplanar rings and the detailed local geometry of acid sites.

Conclusion

A detailed characterization of acid sites in two structurally related zeolites, ferrierite and SUZ-4, is carried out using FTIR spectroscopy. In ferrierite, at least four types of bridging OH groups vibrating in 10-, 8-, and 6-membered rings are identified using a combination of experimental and computational techniques. Our results suggest that aluminum substitution in ferrierite preferentially occurs in extended rings at the intersections of 8- and 6-ring channels, resulting in a high concentration of OH groups in the large cages in 8-ring channels. The IR band corresponding to these hydroxyls, at 3601 cm^{-1}, is not significantly shifted to low frequencies because the OH groups are vibrating in extended rings, although access to these hydroxyls is restricted by 8-membered rings. The band at 3565 cm^{-1} assigned to the bridging OH groups located in 6-membered rings is responsible for the strongly asymmetric shape of the experimental spectrum in ferrierite.

For SUZ-4 zeolite, decomposition of the spectrum, supported by H−D exchange and accessibility studies, gives three IR bands at 3560, 3592, and 3610 cm^{-1} attributed to OH groups in 6-, 8-, and 10-membered rings. The intensity of the first band is considerably lower than that of the corresponding band in ferrierite, indicating that the residual potassium cations are located in small cages or in double 6-rings. The low-intensity band at 3560 cm^{-1} and the similar intensities of the bands at 3592 and 3610 cm^{-1} result in a nearly symmetrical shape for the experimental spectrum.

Finally, assignment of OH groups observed in the spectra of multichannel zeolites requires detailed information on their structure, composition, and aluminum distribution. The simple electrostatic approach relating the value of bathochromic shifts for OH bands to the dimensions of a ring accommodating the hydroxy group can be used for qualitative analysis of complex IR spectra. However, our results suggest that this model should be extended to take into account the exact shape of nonplanar rings and detailed local geometry of acid sites.

References and Notes

(1) Breck, D. W. *Zeolite Molecular Sieves*; Wiley: New York, 1974.

(2) Moscou, L. *Stud. Surf. Sci. Catal.* **1989**, *58*, 1.

(3) Iwamoto, M. *Stud. Surf. Sci. Catal.* **1994**, *B84*, 1395.

(4) Gramlish-Meier, R. *Z. Kristallogr.* **1986**, *177*, 237.

(5) Kibby, C. L.; Perrotta, A. J.; Massoth, F. E. *J. Catal.* **1974**, *35*, 256.

(6) Sheddon, D. *J. Catal.* **1986**, *98*, 1.

(7) Mooiweer, H. H.; de Jong, K. P.; Kraushaar-Czarnetzki, B.; Stork, W. H. J.; Krutzen, B. C. H. *Stud. Surf. Sci. Catal.* **1994**, *C84*, 2327.

(8) Xu, W.; Yin, Y.; Suib, L. S.; Edwards, J. C.; O'Young, C. *J. Catal.* **1996**, *163*, 232.

(9) Barri, S. I. U.S. Patent 5118483, 1992.

(10) Schlenker, J. L.; Higgins, J. B.; Valocsik, E. W. *Zeolites* **1990**, *10*, 293.

(11) Lawton, S. L.; Bennett, J. M.; Schlenker, J. L.; Rubin, M. K. *J. Chem. Soc., Chem. Commun.* **1993**, 894.

(12) Ward, J. W. In *Chemistry and Catalysis by Zeolites*, Version 1; Rabo, J. A., Ed.; Washington, 1976; p 118.

(13) Karge, H. *Stud. Surf. Sci. Catal.* **1991**, *65*, 133.

(14) Kazansky, V. B.; Borovkov, V. Yu.; Kustov, L. M. *Proc. Int. Congr. Catal., 8th* **1984**, *3*, 3.

(15) Jacobs, P. A.; Mortier, W. J. *Zeolites* **1982**, *2*, 226.

(16) Zholobenko, V. L.; Makarova, M. A.; Dwyer, J. *J. Phys. Chem.* **1993**, *97*, 5962.

(17) Wakabayashi, F.; Kondo, J.; Wada, A.; Domen, K.; Hirose, C. *J. Phys. Chem.* **1993**, *97*, 10761.

(18) Boriga, S.; Lamberti, C.; Geobaldo, F.; Zecchina, A.; Palomino, G. T.; Arean, C. O. *Langmuir* **1995**, *11*, 527.

(19) Meier, W. M.; Olson, D. H.; Baerlocher, Ch. *Atlas of Zeolite Structure Types*, Elsevier: Amsterdam, 1996.

(20) Lukyanov, D. B.; Zholobenko, V. L.; Dwyer, J.; Barri, S. A. I.; Smith, W. J. *J. Phys. Chem.,* submitted.

(21) Makarova, M. A.; Garforth, A.; Zholobenko, V. L.; Dwyer, J.; Earl, G. J.; Rawlence, D. *Stud. Surf. Sci. Catal.* **1994**, *A84*, 365.

(22) Treacy, M. M. J.; Higgins, J. B.; von Ballmoos, R. *Collection of Simulated XRD Powder Patterns for Zeolites*; Elsevier: Amsterdam, 1996.

(23) Engelhardt, G. *Stud. Surf. Sci. Catal.* **1991**, *58*, 285.

(24) Stöcker, M. *Stud. Surf. Sci. Catal.* **1994**, *85*, 429.

(25) Naber, J. E.; de Jong, K. P.; Stork, W. H. J.; Kuipers, H. P. C. E.; Post, M. F. M. *Stud. Surf. Sci. Catal.* **1994**, *C84*, 2197.

(26) Eder, F.; Stockenhuber, M.; Lercher, J. A. *J. Phys. Chem. B* **1997**, *101*, 5414.

(27) Moser, W. R.; Chiang, C. C.; Thompson, R. W. *J. Catal.* **1989**, *115*, 532.

(28) Kazanskii, V. B. *Kinet. Catal.* **1982**, *23*, 1131.

(29) Morris, R. E.; Weigel, S. J.; Henson, N. J.; Bull, L. M.; Janicke, M. T.; Chmelka, B. F.; Cheetham, A. K. *J. Am. Chem. Soc.* **1994**, *116*, 11849.

(30) Takaishi, T.; Kato, M.; Itabashi, K. *Zeolites* **1995**, *15*, 21.

(31) Zholobenko, V. L.; Kustov, L. M.; Borovkov, V. Yu.; Kazansky, V. B. *Zeolites* **1988**, *8*, 175.

(32) Klyachko, A. L.; Kapustin, G. I.; Brueva, T. R.; Rubinstein, A. M. *Zeolites* **1987**, *7*, 119.

(33) Bates, S. P.; van Well, W. J. M.; van Santen, R. A. *J. Phys. Chem.* **1996**, *100*, 17573.

(34) Paze, C.; Bordiga, S.; Lamberti, C.; Salvalaggio, M.; Zecchina, A. *J. Phys. Chem. B* **1997**, *101*, 4740.

(35) Fripiat, J. G.; Galet, P.; Delhalle, J.; Andre, J. M.; Nagy, J. B.; Derouane, E. G. *J. Phys. Chem.* **1985**, *89*, 1932.

(36) Blanco, F.; Urbina-Villalba, G.; de Agudelo, M. M. R. *Mol. Simul.* **1995**, *14*, 165.

(37) Jousse, F.; Leherte, L.; Vercauteren, D. P. *Mol. Simul.* **1996**, *17*, 175.