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IR spectroscopic investigation of internal silanol groups in different zeolites with pentasil structure

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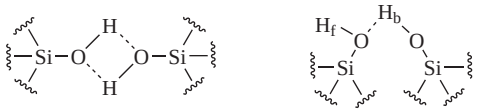
Various isomorphically substituted high-silica zeolites, including ZSM-5, beta, ferrisilicates, gallosilicates and borosilicates, were investigated by diffuse reflectance IR spectroscopy. The narrow band at 3735 cm^{-1} and the broad band at 3500 cm^{-1} were assigned to internal silanol groups. These defect sites in the as-synthesized Na-forms of zeolites arise during the template decomposition.



Two types of internal silanol groups

Keywords: pentasil zeolites, internal silanol groups, diffuse reflectance IR spectroscopy, silicalite, ZSM-5 zeolite, isomorphous substitution, beta zeolite, ferrisilicate, gallosilicate, borosilicate.

Although the hydroxyl groups in zeolites with the MFI structure, including zeolites ZSM-5, as well as ZSM-5 with pentasil structures substituted with boron, gallium and iron, have been investigated in sufficient detail,[1–7] some questions still remain unanswered so far, in particular the nature and properties of so-called 'internal' silanol groups, arising as nests of framework defects during the synthesis of zeolites with high silica content. The existence of these sites has been reported for silicalite and zeolite ZSM-5.[8–13] The band at 3500 cm^{-1} in the IR spectra has been assigned to the stretching vibrations of these hydroxyl groups.[13–15] Using ^{1}H MAS NMR spectroscopy, Hunger *et al.*[16] found an extremely high concentration of silanol groups in ZSM-5 zeolite synthesized in the presence of tetrapropylammonium bromide (Pr_4NBr). The vicinal arrangement of these groups was assumed.

The investigation of these defects is of fundamental interest and associated with optimizing the synthesis of zeolites, the stability of the framework and the performance characteristics of zeolites as catalysts and adsorbents.

In this work, using diffuse reflectance IR spectroscopy, we investigated various high-silica MFI-type zeolites with the pentasil structure, containing Al, Fe, Ga and B, in terms of their appearance, thermal stability and possible structures formed by internal silanol groups.†

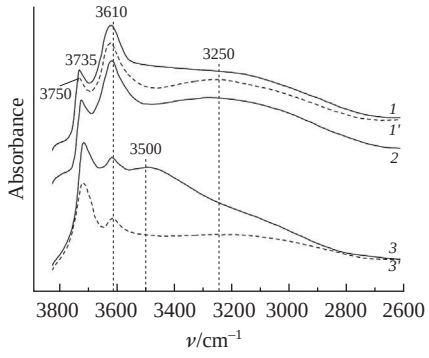


Figure 1 Diffuse reflectance IR spectra of H-[Al]ZSM-5 zeolites synthesized in the (*1*),(*1′*) presence and (*2*) absence of the Pr_4NBr template and (*3*),(*3′*) silicalite-1. The samples were pretreated at (*1*)–(*3*) 770 or (*1′*),(*3′*) 920 K *in vacuo*.

IR spectra of OH groups in various high-silica zeolites, including H-[Al]ZSM-5 zeolites synthesized in the presence or absence of the template (Pr_4NBr), and silicalite are presented in Figure 1. For all zeolites, a band characteristic of isolated bridging hydroxyl groups is observed at 3610 cm^{-1}. As expected, its intensity depends on the aluminum content in the framework. There is also a broad band at 3250 cm^{-1}, which has a relatively high intensity for HZSM-5 zeolites with Si/Al ~20–40 and is visible only as a shoulder in the spectra of silicalite. According to our previous investigations,[13] this band should be attributed to the bridging hydroxyls, which form a strained hydrogen bond with the neighboring oxygen anion of the framework in fragments characterized by large Si–O–Al angles. The narrow line at 3735–3745 cm^{-1} corresponds to the terminal Si–OH groups.

The spectra of the investigated zeolites contain an additional band at 3500 cm^{-1}, which is the most intense for silicalite. Comparing the spectra of HZSM-5 zeolites synthesized with and without a template, we can conclude that the sample synthesized without a template has a lower concentration of hydroxyls, giving

† The synthesis of ferrisilicate samples was carried out at 443 K for 48 h according to the known method.[17] Standard procedures including removal of the template (Pr_4NBr), exchange of Na^+ ions for NH_4^+ ions and subsequent calcination at 770 K for 2 h in the air were applied to obtain the Na and H forms of the samples used in this study. Samples containing Ga and B were obtained similarly. Both isomorphically substituted zeolites, including [Al]ZSM-5, [Fe]ZSM-5, [Ga]ZSM-5 and [B]ZSM-5, and silicalite-1 used for comparison were characterized by XRD and exhibited perfect MFI structure and crystallinity degree close to 95%. Na- and H-forms of zeolites ZSM-5 (Si/Al = 21–250), [Fe]ZSM-5 (Si/Fe = 32–122), [Ga]ZSM-5 (Si/Ga = 13–97) and [B]ZSM-5 (Si/B = 30) and silicalite-1 (Snamprogetti, Si/Al = 250) were calcined at 770 K in air flow for 8 h, followed by pretreatment *in vacuo* at 770 or 920 K for 5 h. Diffuse reflectance IR spectra were measured at 300 K on a Perkin-Elmer 580B spectrometer and an IRF-180 Fourier-transform spectrometer.

a band at 3500 cm^{-1}, relative to the sample obtained by the standard synthesis in the presence of quaternary ammonium compounds. However, Kraushaar[18] found no connection between the high concentration of structural defects and the use of Pr_4N^+ templates. It has been suggested that the formation of structural defects may depend on the crystallization mechanism, which can be influenced by impurities, for instance, in a silica source.

Calcination of the HZSM-5 zeolite at a higher temperature (>870–920 K) leads to the disappearance of this broad band (3500 cm^{-1}). Simultaneously, the band at 3735 cm^{-1} shifts to 3745 cm^{-1}, and its intensity decreases. It follows from these data that isolated Si–OH groups are obviously not homogeneous.

The IR spectra of OH groups in the isomorphically substituted zeolites are shown in Figure 2. The bands of bridging OH groups discussed above are observed at 3628 and 3618 cm^{-1} for H-ferrisilicates and H-gallosilicates, respectively, and in the range of 3300–3350 cm^{-1} for both types of zeolites. As in the case of aluminosilicates with the MFI structure, an additional broad band appears at 3500 cm^{-1}. The narrow band assigned to the silanol groups exhibits a maximum at 3735 cm^{-1}. In the spectrum of ferrisilicate measured with an FTIR spectrometer (Figure 3), this band is resolved into two different narrow peaks at 3730 and 3745 cm^{-1}, which confirms the above assumption about the heterogeneity of isolated silanol groups.

Vacuum pretreatment of ferri- and gallosilicates at 870 K leads to the disappearance of both a broad band at 3500 cm^{-1} and a narrow line at 3730 cm^{-1} or a shift of its maximum to 3745 cm^{-1} (see Figure 2), as in the case of HZSM-5 zeolites. At the same time, another broad band at about ~3300 cm^{-1}, caused by bridging OH groups linked by hydrogen bonds with neighboring oxygen atoms in the framework,[13] remains in the spectra up to sufficiently high pretreatment temperatures (T > 920 K).

For H-borosilicate, the spectrum contains only a broad band at 3500 cm^{-1} and a narrow line at 3745 cm^{-1} (see Figure 2). After high-temperature treatment of borosilicate (870 K), only hydroxyl groups, characterized by a broad band at 3500 cm^{-1}, could be eliminated.

In the case of Na-ferrisilicates synthesized with a template, IR spectra (see Figure 3) were measured before and after ion exchange with Na ions. The spectrum of Na-ferrisilicate before ion exchange contains a low-intensity line at 3628 cm^{-1}, a high-intensity

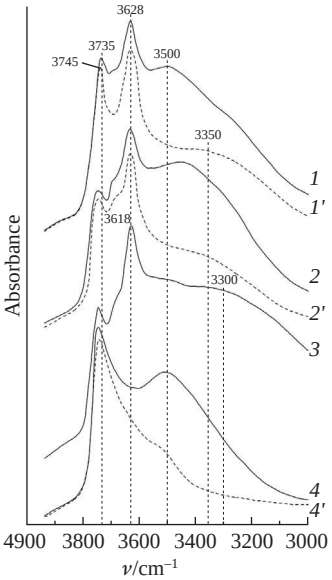


Figure 2 Diffuse reflectance IR spectra of (*1*),(*1′*) H-[Fe]ZSM-5 (Si/Fe = 39.5), (*2*),(*2′*) H-[Fe]ZSM-5 (Si/Fe = 73), (*3*) H-[Ga]ZSM-5 (Si/Ga = 56) and (*4*),(*4′*) H-[B]ZSM-5 (Si/B = 30) pretreated at (*1*)–(*4*) 720 or (*1′*),(*2′*),(*4′*) 870 K *in vacuo*.

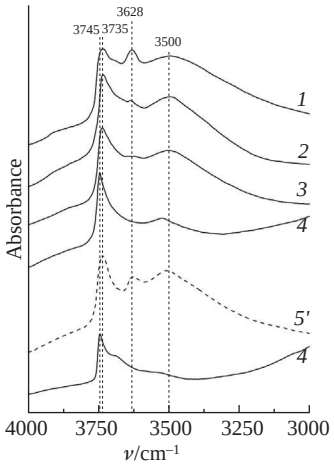


Figure 3 DRIFT spectra of Na,H-[Fe]ZSM-5 with the Na_2O/Fe_2O_3 ratio of (*1*) 0.6, (*2*) 0.8, (*3*) 1.0, (*4*) 2.5 and (*5*) 3.4 before and (*5′*) after ion exchange with NH_4NO_3.

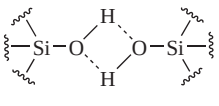
broad band at 3500 cm^{-1} and the silanol group band at 3735 cm^{-1}. After ion exchange for Na^+, the intensity of the peak corresponding to bridging hydroxyl groups at 3628 cm^{-1} decreases, while that of the band at 3500 cm^{-1} remains unchanged. With a decrease in the Na_2O/Fe_2O_3 ratio, the narrow band at 3745 cm^{-1} shifts to 3735 cm^{-1} and a broad band appears at 3500 cm^{-1}. In the case of sodium deficiency (Na_2O/Fe_2O_3 < 1), both a low-intensity band at 3628 cm^{-1} and a high-intensity broad band at 3500 cm^{-1} are observed in addition to a narrow band of silanol groups at 3735 cm^{-1}. After ion exchange of Na^+ ions for NH_4^+ ions and further calcination, the intensity of the band corresponding to bridging hydroxyl groups at 3628 cm^{-1} increases, as well as that of the band at 3500 cm^{-1} (see Figure 3, spectrum *5′*).

Two main conclusions follow from these data. First, hydroxyl groups responsible for the appearance of a broad band at 3500 cm^{-1} in the spectra of zeolites cannot participate in ion exchange either because of non-acidic or weakly acidic nature of these OH groups or because of their inaccessibility to Na^+ cations. Second, this type of OH group appears in zeolites during the synthesis of Na-forms and further decomposition of the template, and not at the stage of decationization by ion exchange for ammonium ions followed by thermal treatment.

In addition, OH groups with stretching vibrations at 3735 and 3500 cm^{-1} seem to belong to the same type of structural defects since the intensities of these two bands vary in parallel.

In our opinion, the above data can be explained by assigning a pair of bands – a narrow line at 3735 cm^{-1} and a broad band at 3500 cm^{-1} – to the internal silanol groups, which are formed in the form of defect nests during the synthesis of pentasil-type zeolites in the presence of templates.

For such internal silanols, the following two structures are plausible:



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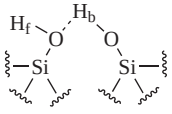

2

Structure **1** includes two equivalent OH groups that are hydrogen-bonded to each other. These OH groups appear to have the same broad band at 3500 cm^{-1} in the IR spectra. Structure **2** includes one proton (H_b) participating in the hydrogen bond and one lone proton (H_f); therefore, two nonequivalent bands should appear in the spectra of OH groups. The broad band at 3500 cm^{-1} probably corresponds to the hydrogen-bonded OH_b groups in

structure **2**. The narrow line at 3730–3735 cm^{-1} can be attributed to the stretching vibrations of the OH_f groups in structure **2**. It is slightly shifted compared to isolated silanols (ν = 3745 cm^{-1}), possibly due to the binding of an oxygen atom. This result is consistent with Sauer's *ab initio* quantum-chemical calculations of the structure and properties of hydrogen-bonded silanol pairs.[19] Compared to isolated SiOH groups, the O–H_b distance increases by 1.7 pm, and the O–H_f bond also becomes slightly longer (by 0.3 pm). In addition, the harmonic force constants for stretching the O–H_b and O–H_f bonds are reduced. As a result, the corresponding wavenumbers of OH stretching vibrations in comparison with the wavenumbers of unperturbed (isolated) silanol groups shift to lower values: $\Delta\nu(OH_b)$ = 200 cm^{-1} and $\Delta\nu(OH_f)$ = 35 cm^{-1}.[19] We found similar frequency shifts for two absorption bands with maxima at 3500 and 3735 cm^{-1} ascribed to internal silanol groups. The experimental shifts are equal to 245 and 10 cm^{-1}.

In our opinion, both of these structures can exist in high-silica zeolites. Nevertheless, structure **2** seems to dominate in ferrisilicates and gallosilicates, while structure **1** is probably more characteristic of borosilicates. It should be noted that both types of internal silanol groups have a rather weak acidity compared to bridging OH groups but higher acidity than isolated silanol groups. Therefore, it is unlikely that they will participate in catalytic reactions taking place on zeolites. However, the presence of such defect sites in zeolites and zeolite-like materials can affect the stability and performance of these catalysts.

Thus, the presence of internal silanol groups seems to be a characteristic feature of various high-silica MFI-type zeolites synthesized in the presence of templates. The appearance of these defect sites during synthesis may reflect deviations from the ideal structure of the zeolite and, thus, may cause both higher instability of the framework and unique catalytic properties. Hydroxyl groups, characterized by a broad band at 3500 cm^{-1} in the spectra of zeolites, cannot participate in ion exchange because they are non-acidic or weakly acidic or because they are inaccessible to Na^+ cations. This type of OH groups appears in zeolites during the synthesis of Na-forms with the subsequent decomposition of the template.

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References

1 J. C. Groen, R. Caicedo-Realpe, S. Abelló and J. Pérez-Ramírez, *Mater. Lett.*, 2009, **63**, 1037.
2 T. Taniguchi, Y. Nakasaka, K. Yoneta, T. Tago and T. Masuda, *Microporous Mesoporous Mater.*, 2016, **224**, 68.
3 J. Čejka, R. Millini, M. Opanasenko, D. P. Serrano and W. J. Roth, *Catal. Today*, 2020, **345**, 2.
4 E. Senderov, I. Halasz and D. H. Olson, *Microporous Mesoporous Mater.*, 2014, **186**, 94.
5 X. Meng, Q. Yu, Y. Gao, Q. Zhang, C. Li and Q. Cui, *Catal. Commun.*, 2015, **61**, 67.
6 I. Halasz, E. Senderov, D. H. Olson and J.-J. Liang, *J. Phys. Chem. C*, 2015, **119**, 8619.
7 V. I. Bogdan, A. E. Koklin, I. I. Mishanin, T. V. Bogdan, N. V. Mashchenko and L. M. Kustov, *Mendeleev Commun.*, 2021, **31**, 230.
8 C. Schroeder, C. Mück-Lichtenfeld, L. Xu, N. A. Grosso-Giordano, A. Okrut, C.-Y. Chen, S. I. Zones, A. Katz, M. R. Hansen and H. Koller, *Angew. Chem., Int. Ed.*, 2020, **59**, 10939.
9 T. Li, F. Krumeich, J. Ihli, Z. Ma, T. Ishikawa, A. B. Pinar and J. A. van Bokhoven, *Chem. Commun.*, 2019, **55**, 482.
10 K. Barbera, F. Bonino, S. Bordiga, T. V. W. Janssens and P. Beato, *J. Catal.*, 2011, **280**, 196.
11 F. Yi, Y. Chen, Z. Tao, C. Hu, X. Yi, A. Zheng, X. Wen, Y. Yun, Y. Yang and Y. Li, *J. Catal.*, 2019, **380**, 204.
12 E. A. Paukshtis, M. A. Yaranova, I. S. Batueva and B. S. Bal'zhinimaev, *Microporous Mesoporous Mater.*, 2019, **288**, 109582.
13 V. L. Zholobenko, L. M. Kustov, V. Yu. Borovkov and V. B. Kazansky, *Zeolites*, 1988, **8**, 175.
14 G. L. Woolery, L. B. Alemany, R. M. Dessau and A. W. Chester, *Zeolites*, 1986, **6**, 14.
15 R. M. Dessau, K. D. Schmitt, G. T. Kerr, G. L. Woolery and L. B. Alemany, *J. Catal.*, 1987, **104**, 484.
16 M. Hunger, J. Kärger, H. Pfeifer, J. Caro, B. Zibrowius, M. Bülow and R. Mostowicz, *J. Chem. Soc., Faraday Trans. 1*, 1987, **83**, 3459.
17 R. Szostak, V. Nair and T. L. Thomas, *J. Chem. Soc., Faraday Trans. 1*, 1987, **83**, 487.
18 B. Kraushaar, L. J. M. Van De Ven, J. W. De Haan and J. H. C. Van Hooff, *Stud. Surf. Sci. Catal.*, 1988, **37**, 167.
19 J. Sauer and A. Bleiber, *Catal. Today*, 1988, **3**, 485.

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