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Address: Univerzitetski trg 2 YU-18000 Niš Tel: +381 18 23953, Fax: +381 18 24488
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# INFRARED STUDY OF THE HYDROXYL GROUPS IN SYNTHETIC ZEOLITES: ZSM–5 AND HZSM–5 SILICALITE

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**Branislava Đurić-Stanojević**
**Predrag Dimitrijević**
**Ljubiša Miljković**

Department of Physics, University of Niš, P.O.Box 91, 18001 Niš, Yugoslavia

**Abstract:** The acidic forms of the synthetic high–silica zeolites ZSM–5 and HZSM–5 silicalite have been investigated by infrared spectroscopy, and their OH stretching vibrations have been determined. For ZSM–5 sample two IR bands have been observed: at 3660 $cm^{-1}$ and 3720– 3740 $cm^{-1}$, which correspond to Si–OH–Al groups and hydroxyls at siliceous impurities or terminal silanols on the external surface, respectively. Highly crystalline HZSM–5 zeolite contains only one type of framework hydroxyl group characterized by an IR vibration at ~3660 $cm^{-1}$ therefore with slightly visible 3720 $cm^{-1}$ band. Another IR band at 3470–3520 $cm^{-1}$ in both samples has been assigned to physisorbed water molecules.

## 1. Introduction

Zeolite acidity occurs as a result of the replacement of tetravalent Si atoms by trivalent Al atoms in aluminosilicate framework. Hydroxyl groups with very acid hydrogen represent the source of acidic catalytic activity of zeolites, acting as Bronsted acid centres by reversible transfer of a proton to a sorbed molecule. Besides Bronsted acidity, there is also Lewis acidity and Lewis acid sites related to electrostatic field gradient (which is especially intense in the vicinity of polivalent cations), and vacant oxygen (because of residual positive charge). Since the importance of Lewis acidity in catalytic processes is much less than that of Bronsted acidity, it can be considered as "by–product" of protonic acidity, because each Lewis acid site is formed from two Bronsted sites during dehydroxylation at high temperatures.

Hydroxyl groups in different positions with respect to local structure in the zeolite framework are that part of zeolite structure which takes part in various catalytic reactions. They are linked either to lattice cations (Si and Al) or to zeolite cations, acting as more or less strong Bronsted acid sites. Different OH groups, their accessibility, coordination (number of nearest neighbours) and their behaviour are the subject of scientific researches for a long time.

Infrared spectroscopy is the most applied method in the characterization of hydroxyls because it reveals some special bands corresponding to the OH groups vibrating in various

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zeolite cavities [1]. Typical wave numbers of the hydroxyl bands lie between 3200 and 3850 $cm^{-1}$.

In order to correlate the nature and positions of some OH groups in the aluminosilicate framework with specific infrared vibrations, we have recorded the IR spectra of high−silica zeolites ZSM−5 and HZSM−5 silicalite in the hydroxyl region between 3000 and 4000 $cm^{-1}$. Obtained spectra show the existence of structural framework hydroxyls in both samples ($\sim$ 3660 $cm^{-1}$), while the ZSM−5 sample of poorer quality contains a second hydroxyl band at 3720−3740 $cm^{-1}$ which has to be assigned to extraneous impurities and external silanols. IR band around 3500 $cm^{-1}$ for both samples originates from physisorbed water molecules.

## 2. Experimental

*Materials and apparatus*

Zeolite ZSM−5 and its protonated form HZSM−5 silicalite are the members of pentasil zeolite group [2] with new configuration in linking $SiO_4$ and $AlO_4$ tetrahedra which consists of eight 5−membered rings of oxygen atoms.

Three-dimensional channel system (3−D) defined by somewhat elliptical tenmembered rings of tetrahedra, contains orthogonal intersections of straight [010] and sinusoidal [100] channels [2]. The "free" channel cross−sections are essentially identical for ZSM−5 and HZSM−5 silicalite. Their dimensions are: 0.54±0.02 $nm$ for nearly circular cross−sectioned sinusoidal (zig−zag) channels and 0.57−0.58 $nm$ × 0.51−0.52 $nm$ for elliptical cross−sectioned straight channels [3]. The channel intersections have a critical dimension of nearly 0.9 $nm$ [4].

A Perkin Elmer Specord 75 IR spectrometer was used for recording the IR spectra of hydrated ZSM−5 and HZSM−5 samples. These samples were present in the form of a self−supporting thin wafers (5 $mg$ zeolite and 150 $mg$ KBr). The OH stretching spectra were scanned at sample temperature of 298 $K$ and at normal atmospheric pressure.

## 3. Results and discussion

The hydroxyl spectrum of the hydrated ZSM−5 zeolite is shown in Figure 1.*a*). A hydroxyl band centered around 3660 $cm^{-1}$ is found. The spectrum of this sample includes a second band at 3720−3740 $cm^{-1}$ as well. Similar two−band spectra already have been appeared in the literature [5].

The presence of physisorbed water molecules is detected by 3470−3520 $cm^{-1}$ band. The same band can be observed in the hydroxyl spectrum of HZSM−5 silicalite sample, (Figure 1.*b*)) with somewhat greater intensity.

Furthermore, the IR band centered about 3660 $cm^{-1}$ can be seen again. The absence (or very low intensity) of band at 3720−3740 $cm^{-1}$ is indicative of highly crystalline materials with negligible amounts of terminal silanols (due to the large crystal size) or extralattice OH groups. Thus the appearence of this band for ZSM−5 zeolite points out a lower quality of this sample, in comparison with HZSM−5 silicalite.

Characteristic vibrations of framework OH groups from Bronsted acid sites (Si−OH −Al) are placed around 3660 $cm^{-1}$ for both samples. The rather high width of this IR band is most probably the result of a slightly differing chemical environment. Indeed, considerable gradients of the Al concentration throughout the crystals of these materials have been reported [5].

The existence of only a single framework OH vibration means that the hydroxyls are vibrating inside the small cages formed at the channel intersections [5,6,7].

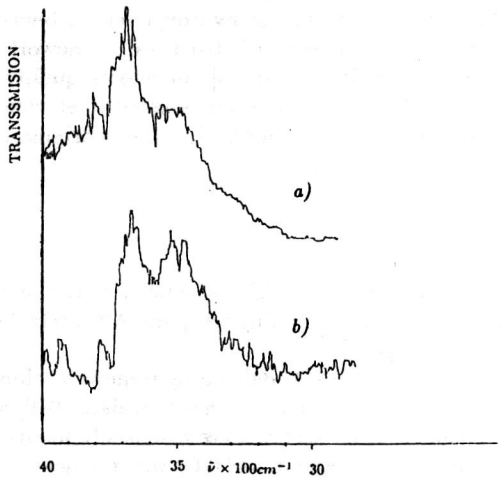


**Figure 1.** Hydroxyl spectra of a) ZSM–5 and b) HZSM–5 silicalite

## 4. Conclusions

Infrared spectroscopy was used to characterize acidic hydroxyl groups in synthetic zeolites having a high Si/Al ratio: ZSM–5 and its protonated form HZSM–5 silicalite. The infrared band at 3660 $cm^{-1}$ is characteristic of strong Bronsted sites for both samples. These active sites are very probably located near the channel intersections. The second IR band at 3720–3740 $cm^{-1}$ (observed in ZSM–5 sample) corresponds to hydroxyl groups of lower acidity. It is assigned to terminal silanol groups (3740 $cm^{-1}$) on the surface of the zeolite or extralattice OH groups (3720 $cm^{-1}$). Its intensity should decrease with increasing crystal size or crystallinity and decreasing amounts in aluminosilicate of siliceous impurities. The absence of this band in hydroxyl spectrum of HZSM–5 silicate indicates that this zeolite sample is a high crystalline material. Finally, the 3470–3520 $cm^{-1}$ band corresponds to nonframework OH groups, e.i. to physisorbed water molecules.

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## PROUČAVANJE HIDROKSILNIH GRUPA U SINTETIČKIM ZEOLITIMA ZSM–5 i HZSM–5 SILIKALITU PRIMENOM INFRACRVENE SPEKTROSKOPIJE

B. Djurić–Stanojević, P. Dimitrijević, Lj. Miljković

**Sadržaj:** Infracrvenom spektroskopijom su proučavane kisele forme sintetičkih, silicijumom obogaćenih zeolita ZSM–5 i HZSM–5 silikalita. Odredjene su vibracije njihovih OH grupa. Kod ZSM–5 uzorka opažene su dve IC trake: na 3660 $cm^{-1}$ i na 3720–3740 $cm^{-1}$, koje odgovaraju Si–OH–Al grupama i hidroksilima na nečistoćama ili terminalnim silanolnim grupama na spoljašnjoj površini, respektivno. Jako kristalan HZSM–5 zeolit sadrži samo jedan tip mrežnih hidroksilnih grupa okarakterisanih IC vibracijama na ~3660 $cm^{-1}$, pa je zato traka na 3720–3740 $cm^{-1}$ slabo izražena. IC traka opažena kod oba uzorka na 3470–3520 $cm^{-1}$ pripisuje se fizički adsorbovanim molekulima vode.