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# Analysis of Active Site Distribution in ZSM-5 Crystals by Infrared Microscopy

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The acid site distribution over large ZSM-5 crystals was analyzed using FTIR microscopy. Results of the analysis of the OH-stretching vibrations and of vibrations of pyridine adsorbed on Brønsted and Lewis acid sites were found to be in good agreement. The resolution which can be obtained using this novel technique is about 10–20 μm. This limits the application to large crystals as analyzed in this study. Comparison of the results of IR microscopy with aluminum distributions obtained by electron microprobe analysis revealed that IR microscopy cannot resolve inhomogeneities on a scale smaller than the above-stated limits. The results of both methods on a larger scale, however, are in very good agreement. Using a combination of both techniques, it is possible to obtain a clearer picture of the distribution of acid sites in large zeolite crystals, where electron microprobing gives the higher resolution, and IR microscopy allows the determination of the types of aluminum site present in the zeolite spatially resolved. © 1993 Academic Press, Inc.

## INTRODUCTION

The acidity of zeolites, one of their most important features with respect to catalytic applications, is created by the presence of trivalent atoms, mostly aluminum, in the lattice. However, the catalytic performance of a zeolite can be strongly influenced by the spatial distribution of the acidic sites over the crystal, depending on the relative values of reaction rates and diffusivities: If acid sites are located in the center of the crystal, the shape selectivity will be good, but the efficiency might be bad due to transport limitations. If, on the other hand, the acid sites are located on the external surface of the crystals, the shape-selective properties tend be poor, since the effect of the narrow pore system of the zeolite is only small. Due to this fact, however, transport limitations are not likely to occur, thus yielding a very efficient catalyst.

The aluminum distribution over ZSM-5 crystals has thus long been of interest. First experimental results were published by Suib *et al.* (*1*), who compared surface composition analyzed by Auger spectroscopy with bulk composition analyzed by conventional chemical analysis. In the following years a number of publications appeared (*2–14*), a great part of which has been reviewed by Jacobs and Martens (*15*). In these studies different types of aluminum zoning have been reported, ranging from enrichment in the outer shell over flat profiles to enrichment in the crystal centers. The distributions were analyzed either by electron microprobing (*2–4*, *14*) or surface analytical techniques (*1*, *5–13*). The methods applied, however, have one common feature: analyzed are the aluminum distributions which do not necessarily coincide with the distributions of acidic sites. Aluminum can be present in a zeolite on lattice positions, creating a Brønsted acid site, or in nonframework or oxygen defect positions, creating a Lewis acid site or no acidity at all, if bulk alumina is present. Although also bulk alumina can be acidic to some extent, not every aluminum atom creates an acidic acid in this

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case. The aluminum distribution thus only reflects the acid site distribution in such cases where all aluminum is in framework positions. This has therefore to be ensured by a separate set of experiments, i.e., MAS NMR spectroscopy.

Here we describe a method which allows the analysis of the distribution of *acidic* sites which is for catalytic applications more relevant than the aluminum distribution. This method employs a relatively novel technique in zeolite science, i.e., IR microscopy (*16–18*). Using IR microscopy, the OH-stretching vibrations as well as the vibrations of pyridine adsorbed on acidic sites which allow discrimination between Brønsted and Lewis acidity, can be analyzed quantitatively with a spatial resolution of about 10–20 μm. A related experiment has been described by van Bekkum and coworkers (*16*), who first used an IR-microscope in zeolite science: they analyzed the 980-cm$^{-1}$ lattice vibration of a boron-substituted ZSM-5 crystal flake spatially resolved to obtain information on the boron distribution. Such an experiment, however, only reveals information also accessible by other methods, although microprobing, for instance, is almost impossible in the case of boron.

## EXPERIMENTAL

The crystals used in this study were synthesized by U. Müller following a procedure based on an ammonia system described elsewhere (*19*). The crystals are about 220 × 60 μm large; the Si/Al ratio determined by XRF is 24. A picture of the crystals as seen in the visible light mode through the IR microscope is shown in Fig. 1. Prior to analysis the crystals were calcined at 823 K for 10 h to obtain the H-form. Since the crystals had been synthesized without alkali, no ion exchange was necessary.

IR spectra were recorded on a SpectraTec Research Plan microscope attached to a Nicolet 5SXB-E bench. For analysis of the OH region the crystals were activated for 5 h at 523 K in a heatable high vacuum cell for the microscope which will be described elsewhere (*20*). Spectra of adsorbed pyridine were either recorded also using the cell after activating and saturating the sample with pyridine *in situ*, or in air. In the latter case the crystals were exposed to pyridine after activation at 525 K for 5 h under high vacuum in a separate loading system and subsequently analyzed with the microscope after placing them on a NaCl window. The results of both methods were found to be similar. However, since the spectra recorded using the cell are much noisier due to scattering and reflection losses at the windows, we only show spectra of pyridine loaded samples recorded in air.

For the recording of spatially resolved spectra a rectangular spot of 20 μm along the length of the crystal × 60 μm over the crystals width was selected by means of two adjustable apertures above and below the sample stage. The second aperture increases the resolution by blocking scattered radiation from the first aperture and the sample. The crystal was then moved in steps of about 13 μm through the illuminated area.

To compare the IR microscopic method to a well established technique for analysis of the aluminum distribution, we also analyzed the crystals using a Cameca electron microprobe. Samples were prepared by embedding crystals in an epoxy resin which was subsequently polished with 0.5-μm diamond paste to remove the outer surface. The crystals were analyzed in the step scan mode with a resolution of 1–2 μm.

## RESULTS

Using the high vacuum cell it is possible to obtain high quality spectra of single zeolite crystals, as was already described by Nowotny *et al.* (*17*), who studied the decomposition of template in ZSM-5. Figure 2 shows the spectrum of a ZSM-5 crystal after activation in the vacuum cell measured under high vacuum conditions. The crystal was oriented with the (010) direction parallel to the beam axis. The most prominent band in the OH-stretching region is the 3612-cm$^{-1}$ band

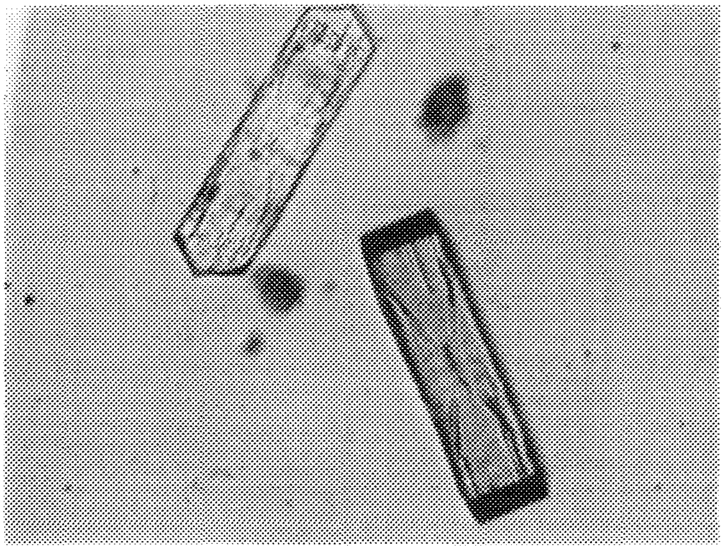

FIG. 1. ZSM-5 crystals analyzed as seen through the IR microscope in visible light mode.

which corresponds to strong Brønsted acidic sites. A very low intensity band can be seen at about 3740 $cm^{-1}$ which can be attributed to silanol groups. The low intensity of the 3740 $cm^{-1}$ indicates that the crystals are relatively free of defects. The noisy background in this spectral region is due to imperfect compensation of gas-phase water in the beam.

If spatially resolved spectra shall be analyzed, it is not sufficient to plot the intensity of the 3612-$cm^{-1}$ band over the crystal length, since at the edges of the crystal less zeolitic material is present in the beam as compared to analysis of the center of the crystal. It is thus necessary to normalize the intensity of the 3612-$cm^{-1}$ band using bands corresponding to vibrations of lattice atoms. We chose the bands between 2118 and 1746 $cm^{-1}$ because this region is fairly unaffected by changes in the composition of the material. Figure 3 shows the ratio of the inte-

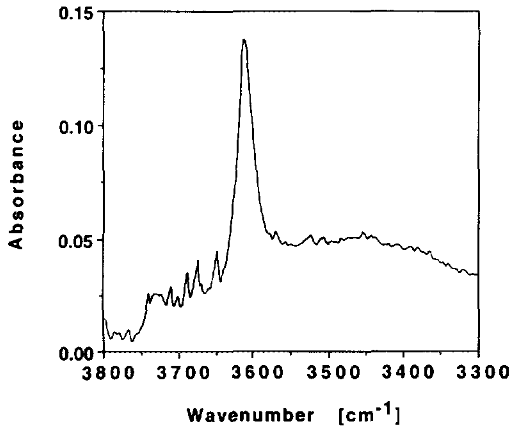

FIG. 2. Spectrum of the OH region of a large ZSM-5 crystal activated at 523 K in high vacuum over 5 h.

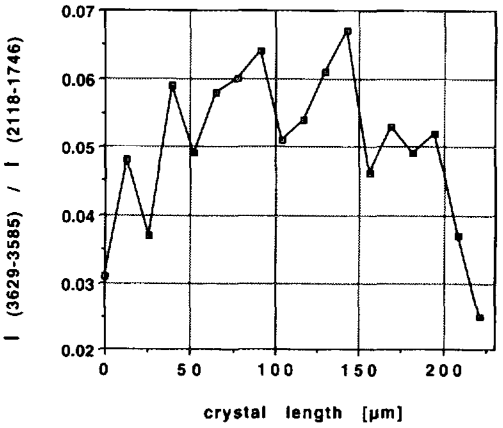

FIG. 3. Normalized intensity of the OH band at 3612 $cm^{-1}$ of a large ZSM-5 crystal along the crystal $c$-axis.

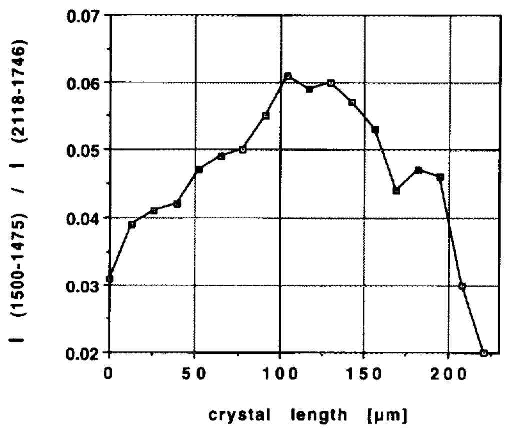

FIG. 4. Normalized intensity of the 1490-cm$^{-1}$ band of pyridine adsorbed on a large ZSM-5 crystal along the crystal $c$-axis.

grated absorbances of the 3612-cm$^{-1}$ band and the above mentioned spectral region, resp., plotted over the position of the IR beam on the crystal. The intensity of the OH band increases by a factor of about two towards the center of the crystal. There is a relatively large scatter in the data which is due to the noisy spectra. It is difficult to overcome this problem without losing resolution, since only little energy throughput can be achieved with a small sampling area and the additional losses brought about by the cell. In addition, there are severe scattering losses near the crystal edges.

One way to overcome this problem is the analysis of bands of adsorbed pyridine instead of analyzing the OH region, since especially the band at 1490 cm$^{-1}$, to which pyridine bonded to Brønsted sites as well as pyridine bonded to Lewis sites contribute, has a large extinction coefficient. The result of such an experiment is depicted in Fig. 4. Also in this case the band intensities were normalized as described above. The results were similar to those obtained from the analysis of the OH region. The concentration of acidic sites is about a factor of 2 higher in the center of the crystal. In this case we analyzed the 1490-cm$^{-1}$ band. There are contributions to the intensity of this band from pyridine adsorbed on Brønsted as well as on Lewis sites. However, the samples analyzed in this study do not contain any Lewis acidity which can be inferred from the absence of the 1455-cm$^{-1}$ band in Fig. 5 which shows the spectrum of a 20 × 60 μm part of the center of the crystal. Also major contributions from hydrogen bonded pyridine to nonacidic species, i.e., silanol groups, can be excluded, since the concentration of silanol groups is very low, as discussed above. It is thus possible to extract the information from the band with the highest intensity which is the one at 1490 cm$^{-1}$. Since the intensity of this band is fairly high, the data in Fig. 4 show much less scatter than the data extracted from the analysis of the OH region presented in Fig. 3. In principle, however, it is certainly possible to analyze pyridine adsorbed on Brønsted and on Lewis acid sites separately, thus allowing the discrimination between these types of sites spatially resolved.

To make sure that the sample was completely saturated with pyridine, the OH region of the pyridine loaded sample was analyzed. For that purpose the pyridine-loaded crystals were activated in the *in situ* high vacuum cell under high vacuum for 3 h at 473 K, well below the desorption temperature of pyridine from Brønsted acidic sites of ZSM-5. No OH band at 3612 cm$^{-1}$ could

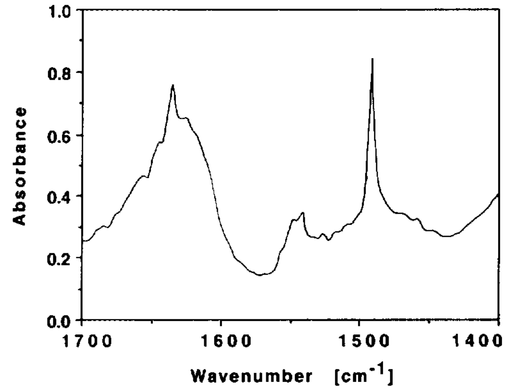

FIG. 5. Spectrum of pyridine adsorbed on a large ZSM-5 crystals. Analysis region 20 × 60 μm in the center of the crystal.

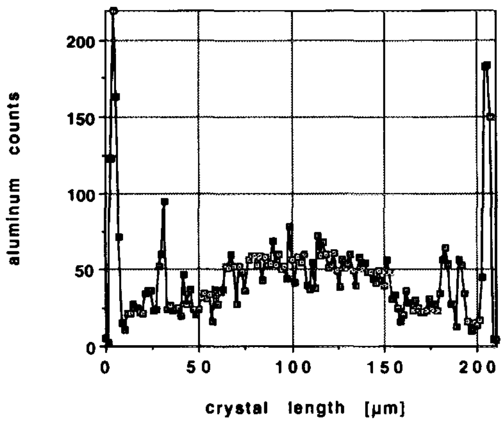

FIG. 6. Aluminum concentration along the $c$-axis of a large ZSM-5 crystal analyzed by electron microprobing.

be observed after this treatment, which indicates complete saturation of the sample with pyridine.

We analyzed several crystals in the OH region as well as with adsorbed pyridine. Profiles as shown in Figs. 3 and 4 were observed for all crystals analyzed. However, the question remains as to how the IR-microscopic analysis of acid site distribution compares to distributions obtained using other techniques. The most reliable method to analyze the spatial distribution of elements over a crystal is electron microprobing. A typical result of such an analysis of a crystal from the same batch as investigated by IR microscopy is shown in Fig. 6. There are sharp aluminum peaks at the very edge of the crystal, which had not been observed using the IR microscope. The formation of such peaks which have been reported before was attributed to the specific interactions between aluminosilicates and template molecules or alkali-cations in the synthesis mixture (*13*). Disregarding these peaks, however, the aluminum concentration increases towards the center of the crystals, as was observed with the IR microscope. Also the microprobe analysis was performed on several crystals which essentially resulted in the same profiles.

## DISCUSSION

On comparing the analysis with the IR microscope and the electron microprobe, the agreement on a large scale is obvious: the concentration of the acidic sites increases towards the center of the crystals. However, strongly localized effects, as the aluminum peaks near the rim of the crystals found using the microprobe, are not observed in the IR microscope. There are, at least, two possible explanations for this fact: (1) the resolution of the microscope is not sufficient to reflect inhomogeneities on a scale smaller than about 10–20 µm, or (2) the aluminum peaks found with the microprobe do not correspond to acidic sites, neither Brønsted nor Lewis sites.

Although we can not definitely prove either of these explanations, there is much more evidence in favor of the first one, the lacking resolution of the IR microscope. One might assume that a strong peak as found with the microprobe should definitely show up in the spatially resolved IR spectra, too, if only somewhat smeared out due to the appreciably lower resolution. One has to keep in mind, though, that near the crystal rims scattering losses are most severe, and that possibly no signal is obtained from the very edges at all where the microprobe showed the aluminum peak. We attempted to reduce the scattering losses by index matching with different hydrocarbons, but that introduces new problems due to the absorption of IR radiation and adsorption of the hydrocarbons in the crystals so that up to now these efforts were without success.

Moreover, there is one fact that would be very difficult to explain if the discrepancy between IR and microprobe profiles were due to the presence of aluminum not leading to any acidity: NMR spectra of the samples only show very minor traces of octahedrally coordinated aluminum. It is difficult to imagine in what form the aluminum would be present in the crystals in tetrahedral coordination without creating an acidic site.

In addition, one should keep in mind that the IR microscope probes a different volume than the electron microprobe: The microprobe analyzes a volume of about 2 × 2 × 2 $\mu$m in the center of the crystal, because the outer surface has been removed by polishing. The IR microscope, on the other hand, analyzes 20-$\mu$m-long slices over the whole width and depth of the crystal. This leads to a higher aluminum background as compared to the microprobe, since also in the crystallographic *a* and *b* directions of ZSM-5 aluminum was found to be enriched towards the rims of the crystals (*21*). This effect leads to an additional reduction of resolution of the IR microscope.

One thus has to conclude that IR microscopy is sufficient for the analysis of large scale inhomogeneities, but fails in detecting structures in the range of 10 $\mu$m or less, especially when these structures are located near the crystal edges where strong scattering occurs. This is certainly a major drawback of this new method compared to electron microprobing. On the other hand, IR microscopy has to offer some advantages: (1) Sample preparation is much easier and less crucial than for the electron microprobe. Embedding and polishing the crystals requires a lot of experience, and a low quality sample preparation for the microprobe can lead to severe artefacts and misinterpretation of the profiles obtained. (2) The most important advantage of the IR technique, especially for catalytic applications, is the fact that IR microscopy in principle allows the determination of the nature of the aluminum species and thus gives access to the catalytically relevant information. IR microscopy and electron microprobing can thus be considered as complementary techniques, one yielding the more detailed information, the other the higher spatial resolution.

IR microscopy seems especially suited for monitoring the effects brought about by different dealumination processes (localization of the dealuminated sites, nature of the species formed) on large ZSM-5 crystals as a model system for other dealumination processes. Work is under way in our laboratory to address these questions using a combination of electron microprobing and IR microscopy.

## SUMMARY

A new method to analyze the spatial distribution of active sites over ZSM-5 crystals using infrared microscopy has been developed. The method allows the analysis of large scale inhomogeneities > 10 $\mu$m, and is in principle able to give spatially resolved information on the types of acidic sites present. For the analysis of inhomogeneities on a smaller scale, however, electron microprobing has to be used as a complementary technique. The ZSM-5 samples analyzed show a strong enrichment of aluminum in the outer shell with a very sharp profile, detected by microprobe, but not by IR spectroscopy. A less pronounced enrichment of aluminum by about a factor of 2 towards the center of the crystals was also observed. IR microscopy showed that this is an inhomogeneity not only in the aluminum concentration but in the acid site concentration as well.

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