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TEM Imaging

Tracking down the secrets of zeolites, a real all-round talent

Structural analysis of zeolites using a combination of highly resolving electron microscopy and digital image processing

Hardly anyone knows what they‘re called. And we use them every day, even though we may not know it. We‘re talking about zeolites, a group of minerals with extraordinary and outstanding properties. Since being discovered in 1756, zeolites have been a focus of research.

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There was a real run on them starting in 1920 once it became possible to decode the crystalline structure of natural zeolites. The new findings were the key to understanding this fascinating materials group and the point of departure for targeted synthesis. The road was opened for numerous application opportunities. And the boom continues. One reason being that zeolites are extremely environmentally friendly and energy efficient. These are highly attractive properties in times when concerns regarding global warming and rising energy costs are widespread. The Max Planck Institute for Coal Research in Mülheim a.d. Ruhr, Germany uses the latest structural analysis methods for understanding zeolites‘ structure and function. Their objective is to synthesize custom-designed crystalline structures in order to employ them for specific catalytic processes.

The great unknown factor

Zeolites? Never heard of them? And yet we all use them practically day-in and day-out. Zeolites make industrial production processes considerably more energy efficient and thus more environmentally friendly. In car catalytic converters for filtering car exhaust, zeolites are used as microsieves for adsorbing any pollutants. Zeolites are crucial for cars. Without them, any conventional car would literally be stuck at the side of the road. Zeolites are of tremendous importance to the petrochemical industry. They serve as catalysts that break down (crack) hydrocarbons into precisely defined lengths to make gasoline and other byproducts. Depending on what end product is desired in the petrochemical industry, a very specific type of zeolite group is used as a catalyst. This determines the length that the resulting hydrocarbon chain will actually have. But zeolites are also used in people‘s day-to-day lives. You have little zeolithic mineral grains softening water when clothes are washed. Kitty litter contains zeolites for binding those substances emitting nasty odors, and every smoker literally chomps on them when they smoke a filter cigarette.

Figure 1: Zeolites have a broad range of applications in our daily lives. Small zeolite mineral grains soften water (see title page) when clothes are being washed. Zeolites also serve as catalysts for cracking hydrocarbons in precisely defined lengths, resulting in gasoline and other substances (links). Zeolites are also used in something completely different – kitty litter. The zeolites bind any unpleasant odors (right).

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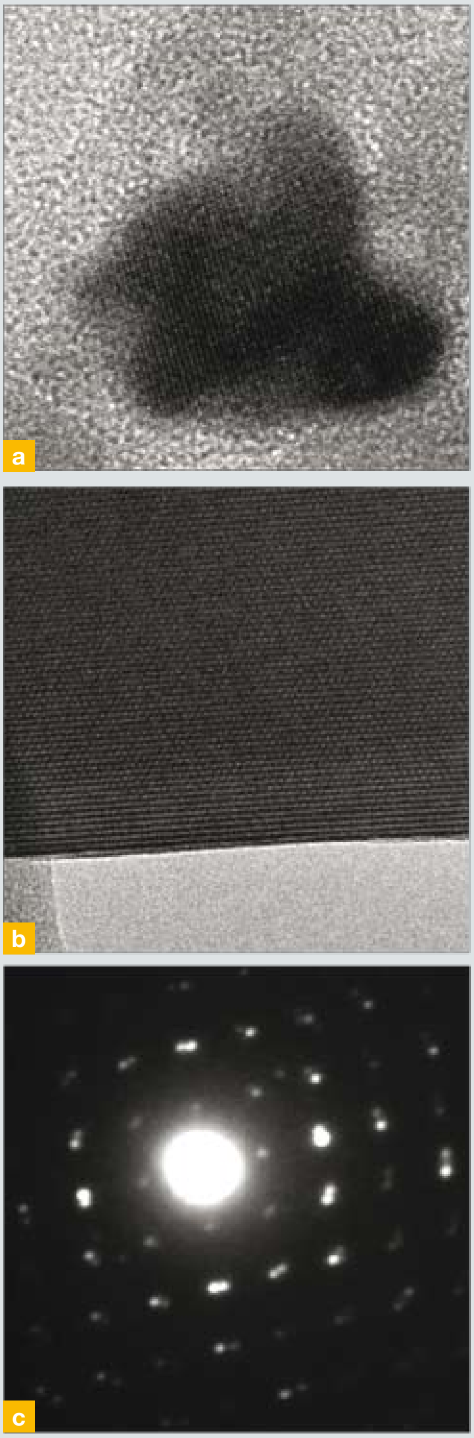


Figure 2: a,b: HRTEM images of the canal structures of typical zeolites. c: An example of a corresponding electron diffraction pattern of image a.

The evaluation of TEM investigations makes it possible to make very detailed, locally precise statements on the form and size of the empty spaces and provides important information on existing structural defects. These defects are of tremendous importance because they can significantly alter the functional capacity of the zeolites. Using these images, the synthesis scientist can directly assess whether the desired structure has crystallized during synthesis. Are the empty spaces that formed of sufficient size for the corresponding cations or molecules to fit, or are there defects impeding the formation of the desired shape? Images acquired with MegaView Camera on a FEI Technai G2 Spirit, using 120 KV. Diameter of crystals is about 20 nm, lenght of image clipping is about 140 nm.

Tracking down answers

But what is it that makes zeolites so special? What makes this group of minerals so interesting that they have the attention of many scientists in modern research institutes? Why are these minerals so omnipresent – gasoline, PET bottles, kitty litter, washing detergent – in so many industrial production processes and day-to-day uses? What properties do zeolites have that ensure they can be used in so many different ways? And what makes them so environmentally friendly?

Answers to these questions are sought by Dr. B. Tesche, head of the department of electron microscopy at the Max Planck Institute for Coal Research in Mülheim a.d. Ruhr, Germany. Tesche has been investigating these questions with his research team for many years. Tesche explains: „Zeolites are sensitive to radiation. But we have developed methods for preparing samples that enable us to investigate the zeolites‘ structure in the electron microscope without any significant radiation damage occurring.“ And this opportunity to look at the crystalline structure is what provides Dr. Tesche „the key to understanding this material group.“ In order to execute the wide range of tasks required for obtaining this understanding, Dr. Tesche‘s workgroup uses highly resolving electron microscopes and the latest software and hardware. Digital image acquisition is done with a KeenView camera by Olympus Soft Imaging Solutions, a special, highly resolving TEM camera mounted on one of Dr. Tesche‘s TEMs. Acquisition control, documentation and analysis is taken care of by iTEM, the TEM image analysis platform.

Of prime interest from the start

Naturally occurring zeolites were discovered and named in 1756 by A.F. von Cronstedt, the Swedish mineralogist. He observed behavior in this previously unknown group of minerals that he described as an apparent simmering. When heated, zeolites release water enclosed in pores. The minerals can easily (and reversibly) release the water within their crystalline structure, without the structure being altered. This is why Cronstedt selected the term „zeolite“ which literally means „simmering stone“ [Greek. zein = to simmer, lithos = stone].

Naturally occurring zeolites form in the late-magmatic hydrothermal range at low temperatures and pressures and require the presence of water or aqueous, alkaline mineral salt solutions. They form in hollow spaces and fissures of basic volcanite or also in crystalline slate and metalliferous veins. About 60 different types of naturally occurring zeolites are known.

In 1920, the crystalline structure of natural zeolites was decoded (see text box: zeolite crystalline structure) using x-ray diffractometry. The matrix of these minerals contains canals and cages throughout which facilitate reversible absorption of the widest variety of molecules. This discovery triggered a veritable research boom. If a specific synthesis of defined pores and canal sizes can be successfully crystallized, a sheer unlimited range of applications would become possible. To this day zeolites are used as ion exchangers, microsieves, drying agents, water softeners, catalysts and for heat storage.

Variation via synthesis

Synthesis has steadily gained in importance – particularly for the industrial sector. To date, there are about 80 different synthetic zeolites that have been produced in the lab. Materials scientists are increasingly able to synthesize zeolites more and more precisely and thus to produce highly interesting substances for new applications. The exact understanding of crystallization conditions is a prerequisite for targeted synthesis. In order to obtain further information, decoding the crystalline structure is decisive for scientists. This can be observed directly using the TEM providing valuable conclusions on synthesis parameters. As Dr. Tesche noted: „If the crystalline structure is understood and compared with the naturally occurring zeolites, conclusions can be drawn on pressure and temperature conditions, on the amount of water required as well as on important structural determinant additives. These structure determinants are usually organic molecules whose size and shape serve as placeholders for the hollow spaces to be synthesized.“ Nature is thus the model for optimal generation of synthetic zeolites under lab conditions. However, there are a great number of synthesis parameters that affect one another making prediction difficult. „Direct observation and decoding of structures is key“, continued Dr. Tesche. Combining up-to-date, highly resolving TEM technology and digital image acquisition provides the ideal tools for assessing whether the synthesis has created the desired crystalline structure.“ Structural details such as the size of the hollow spaces or structural defects that may significantly influence zeolite properties become directly observable.

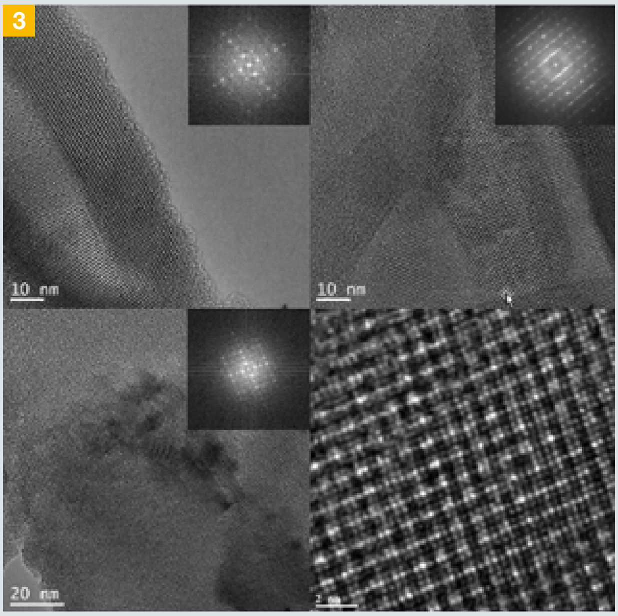


Figure 3: Thin sections of embedded Sn-beta zeolite crystals sandwiched into thin carbon films, Cs-corrected HRTEM images at 80 kV, inserted FT images shown intensities down to the 7th order, corresponding to the resolution of 0,18 nm. Images by B. Tesche, Head of the Department of Electron Microscopy, Max Planck Institute for Coal Research, Mülheim a.d. Ruhr, Germany, B. Freitag, S. Kujawa, FEI Company, Eindoven, Netherlands

On new paths

Synthetically produced zeolites have very small grain sizes and a high density of structural defects. Thus, says Tesche, „conventional investigative methods such as x-ray single-crystal methods or neutron diffraction are of no use for two reasons.“ Because these methods a) require grain sizes of several hundred ångstrom (1å = 10^{-10} m), and b) provide no definite results if the structure has too many defects. Highly resolving transmission electron microscopy, on the other hand, can deliver the desired information. „Structural information on sample areas smaller than 0.4 nm (1 nm = 10^{-9} m) can be procured“, continued Dr. Tesche. In addition, TEM and especially HRTEM are very useful investigative methods for not simply investigating the crystalline structure, but also further microstructural properties such as twins, defect structures and dislocations.

Radiation damage – help wanted – and found

If no particular preparations are made during the investigation in the transmission electron microscope, the zeolites amorphize: ie, the electron beam causes tremendous ionization of the sample material. There are local charges that can lead to the loss of their three-dimensional, strictly periodical structure and even completely destroy them. This naturally means their physical properties are lost. The presence of water molecules and easily volatile cations in conjunction with the aluminum content of the matrix also plays a significant role. One possibility for retaining the structure is by developing suitable sample preparation with high structural conservation. Another possibility involves compensating the interaction of the primary beam with the object atoms.

To reduce radiation damage, Dr. Tesche‘s team did two things. They developed their own sample preparation and make use of modern digital acquisition technology. This enables them to work very efficiently such that images are acquired before the beam has largely destroyed the structure. Another option for preventing radiation damage is to reduce acceleration voltage. However, this means obtaining less information and usually leads to noisy images. „This problem can be sidestepped using very sensitive TEM cameras“, says Tesche. „Cameras like the KeenView we use have an excellent signal/noise ratio even at low acceleration voltages. Structural details, that at high resolution are barely perceptible to the naked eye on the fluorescent screen, can still be resolved by digital cameras.“ Tesche is also enthusiastic about the camera‘s speed. „The camera works so quickly that the image acquisition has already taken place before complete amorphization has destroyed the necessary structural information.“

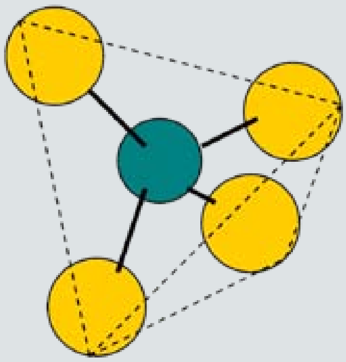
Full evaluation at the PC

The further evaluation of the acquired images is done via a desktop license for the iTEM software which comes with the camera. „For analyzing our electron diffraction patterns we use the iTEM Solution Diffraction, a software extension“, explains Tesche. „This enables us to measure distances and angles very precisely. The indexing of the reflexes takes place automatically.“ Because image acquisition is totally digitized it takes just a few steps to have images acquired, image quality enhanced, structural details evaluated, everything documented and archived – in the comprehensive software solution. This is how the team at the MPI for Coal Research are able to display and evaluate these very complex structures.

The crystalline structure of zeolites

The distinctive characteristic of zeolites are their high degree of variability with regard to chemical composition. In their natural form, the primary building blocks (SiO4) - and (AlO4) – are tetrahedra (fig. 4). In the middle of each tetrahedron there is a Si or Al cation, which is surrounded by 4 oxygen ions at the four corners of the tetrahedron. This always results in a negative charge of the matrix. The cation in the center of zeolites containing no silicate may be beryllium, phosphorus or zinc. The tetrahedra combine to form three-dimensional, strictly periodical components via common oxygen bridges. These represent rings of 4, 6 and 8 and form secondary components.

A microporous tetrahedron matrix with empty spaces of pores, canals and cages throughout results from the linkage in three-dimensional space. Large cations and crystal water in these empty spaces can equalize the negative charge of the matrix. A distinct characteristic of zeolites is the extremely large interior surface (microsieve) and the possibility to reversibly dehydrate and to provide and release cations (ion exchange). In so doing they are not subject to any structural change when pressure and temperature are kept constant in a certain range. Despite the highly porous microstructure, zeolites are extraordinarily stable mechanically and thermically. Due to the critical significance of synthesis with a new and increasing range of compositional combinations, all structures that have the characteristic tetrahedron structure are termed zeolites these days.



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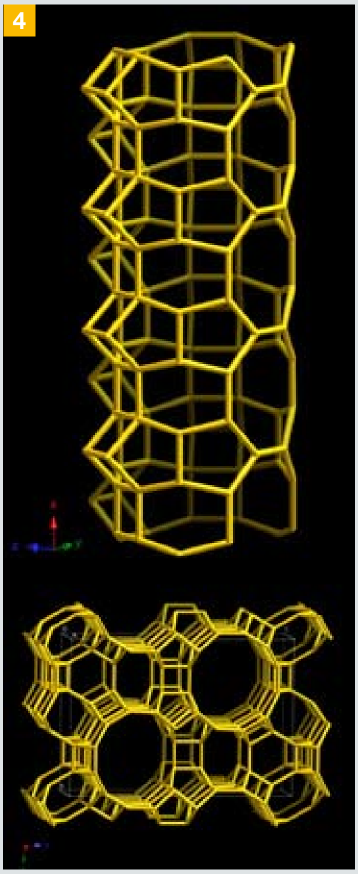

Figure 4: Examples of zeolithe structure. Image Courtesy Ch. Baerlocher and L.B. McCusker, Database of Zeolite Structures: http://www.iza-structure.org/databases/

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