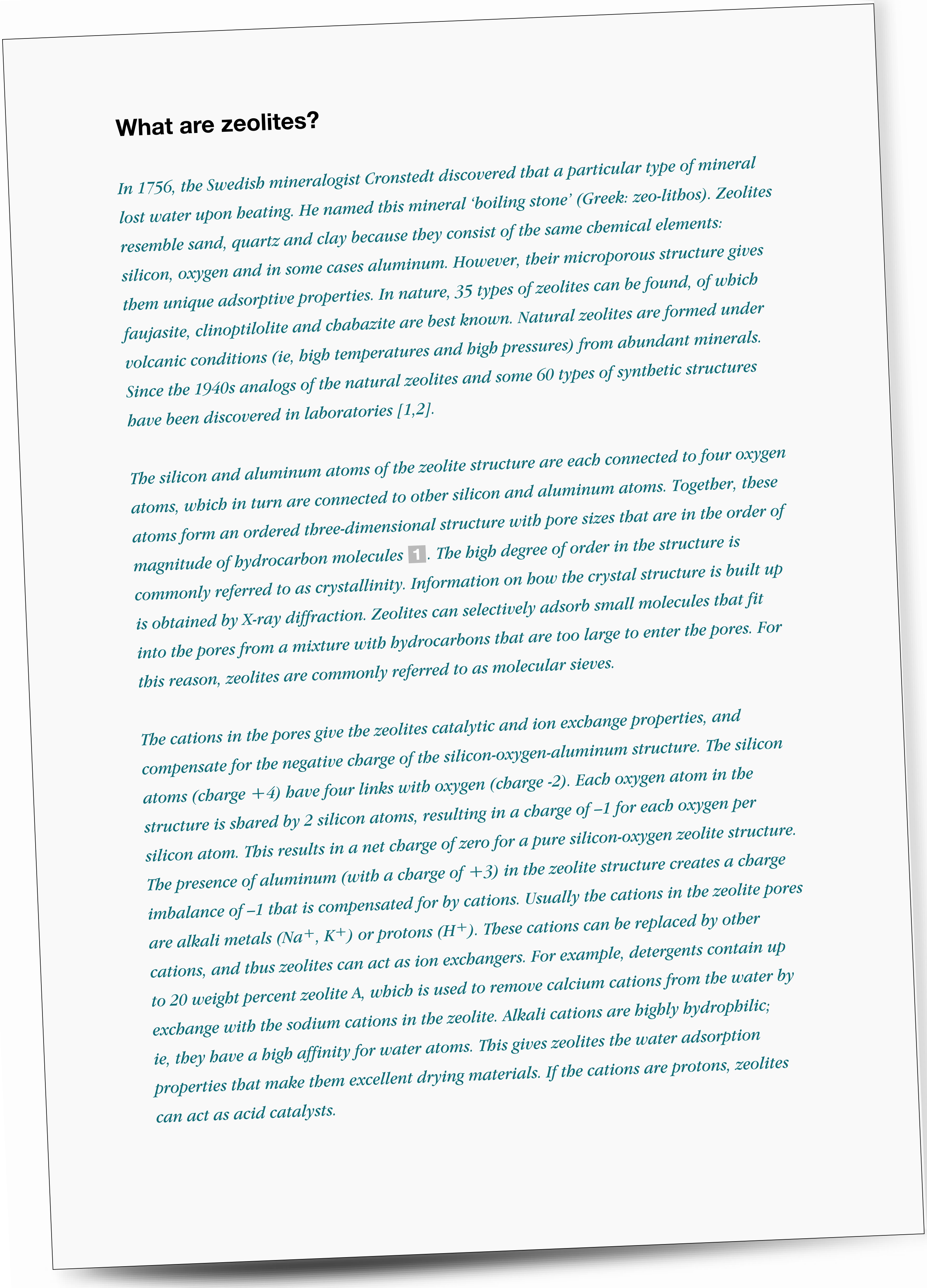
Oil, Gas and Petrochemicals

An innovative zeolite synthesis technology with



What are zeolites?

In 1756, the Swedish mineralogist Cronstedt discovered that a particular type of mineral lost water upon heating. He named this mineral 'boiling stone' (Greek: zeo-lithos). Zeolites resemble sand, quartz and clay because they consist of the same chemical elements: silicon, oxygen and in some cases aluminum. However, their microporous structure gives them unique adsorptive properties. In nature, 35 types of zeolites can be found, of which faujasite, clinoptilolite and chabazite are best known. Natural zeolites are formed under volcanic conditions (ie, high temperatures and high pressures) from abundant minerals. Since the 1940s analogs of the natural zeolites and some 60 types of synthetic structures have been discovered in laboratories [1,2].

The silicon and aluminum atoms of the zeolite structure are each connected to four oxygen atoms, which in turn are connected to other silicon and aluminum atoms. Together, these atoms form an ordered three-dimensional structure with pore sizes that are in the order of magnitude of hydrocarbon molecules 1*. The high degree of order in the structure is commonly referred to as crystallinity. Information on how the crystal structure is built up is obtained by X-ray diffraction. Zeolites can selectively adsorb small molecules that fit into the pores from a mixture with hydrocarbons that are too large to enter the pores. For this reason, zeolites are commonly referred to as molecular sieves.*

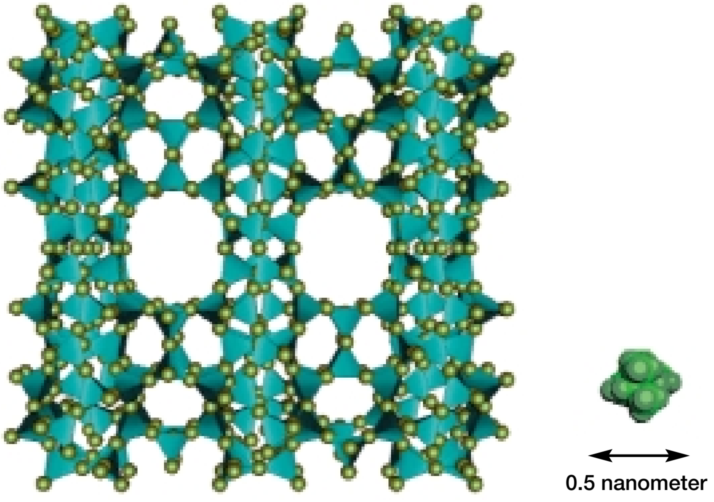
The cations in the pores give the zeolites catalytic and ion exchange properties, and compensate for the negative charge of the silicon-oxygen-aluminum structure. The silicon atoms (charge +4) have four links with oxygen (charge -2). Each oxygen atom in the structure is shared by 2 silicon atoms, resulting in a charge of –1 for each oxygen per silicon atom. This results in a net charge of zero for a pure silicon-oxygen zeolite structure. The presence of aluminum (with a charge of +3) in the zeolite structure creates a charge imbalance of –1 that is compensated for by cations. Usually the cations in the zeolite pores are alkali metals (Na^+, K^+) or protons (H^+). These cations can be replaced by other cations, and thus zeolites can act as ion exchangers. For example, detergents contain up to 20 weight percent zeolite A, which is used to remove calcium cations from the water by exchange with the sodium cations in the zeolite. Alkali cations are highly hydrophilic; ie, they have a high affinity for water atoms. This gives zeolites the water adsorption properties that make them excellent drying materials. If the cations are protons, zeolites can act as acid catalysts.

great promise for the petrochemical world

Nelleke van der Puil, Frits Dautzenberg, Jan Henk Koegler

Zeolites – porous crystalline alumino-silicates – are used as catalysts in many of today's petrochemical processes. An innovative zeolite synthesis procedure has been developed by ABB that improves catalytic performance by creating ultra-small zeolite crystals in an optimized matrix. Demonstrated at a size that allows full scale-up, it offers significant advantages over conventional zeolite synthesis techniques. In laboratory tests, zeolite catalysts prepared using this novel procedure showed improved performance compared with zeolites produced via conventional routes. Another advantage of the new synthesis technology is that it reduces the manufacturing cost of zeolites. Considering the broad application field of zeolites, this technology has the potential of becoming a genuine breakthrough for catalysis in the petrochemical world.

Zeolites are utilized as catalysts in the production of bulk chemicals such as gasoline and styrene, as adsorbents in house-hold applications such as air drying, air filtration ('odor eaters') and water filtration, and as ion exchangers in detergents. ABB Lummus Global developed and licenses various petrochemical and refining processes that make use of zeolite catalysts. These applications benefit from the most important catalytic quality of zeolites: they act as a 'solid acid' catalyst if they contain protons (H^+ ions). The protons catalyze the break-up (cracking), internal changes (isomerization) and coupling (alkylation, oligomerization) of hydrocarbon molecules. Although zeolites are very strong acids, they are non-hazardous materials that can be handled without extensive precautions. In the past decade, many chemical processes have been revamped to replace liquid acid catalysts (sulfuric acid and hydrofluoric acid) that form environmental hazards. Catalyst research at the ABB Lummus Global Technology Development Center in Bloomfield, USA has focused on achieving improvements in alkylation processes not only by process design optimization but also by zeolite catalyst development.



1 Schematic representation of a zeolite structure. The green spheres at the corners of the tetrahedra are the silicon and aluminium atoms. The oxygen atoms, which are not shown, are located at the edges of the tetrahedra and interconnect the silicon and aluminium atoms. Together, these atoms form an ordered 3-D network with well-defined pores of the order of magnitude of hydrocarbon molecules (on right).

Understanding zeolites: a journey into the molecular world

Two important qualities determine the performance of a catalyst: activity and selectivity. These factors are controlled by the chemical and physical properties of the catalyst and by the conditions of the process. While the chemical properties of the catalyst may intrinsically be suitable to carry out a reaction at a high activity and selectivity, the physical properties of the catalyst may limit performance. Zeolites are highly acidic and active and can replace the strongest liquid acids. The size of the zeolite pores is similar to the size of the hydrocarbon reactants and products. This feature is both a blessing and a curse, giving rise to high product selectivity but slowing down reactant conversion. The pore dimensions of zeolites (0.3-0.8 nm, also called micropores) allow highly selective conversions of hydrocarbons by geometric constraints. Approximately 100 different zeolite types exist, each having a different crystal structure and specific pore dimensions. These features of the microporous structure of zeolites result in highly selective reaction pathways, thereby limiting the amount of byproducts and downstream processing cost. However, the same geometric features also work in a negative way: the transport of the molecules in the pores of a solid is much slower than in the liquid phase or the gas phase. In many cases, the rate of transport of reactants and products to and from the catalytic sites determine the rate of the reaction, and the catalyst is not used to its full potential. This is a well-known phenomenon in catalysis that is commonly referred to as 'diffusion limitation'. The transport of molecules can be accelerated if the distance they have to travel through small pores is reduced. Obviously, the geometric constraints on the molecules decrease with increasing pore size. Thus it is of great importance to make smaller zeolite crystals.

The zeolite crystals are always embedded in a matrix material that facilitates materials handling and process operation. This matrix material should contain pores that are sufficiently large to allow fast molecular transport. The larger pores are called mesopores if their size is between 2 and 50 nm, and macropores if they are larger than 50 nm. A linear hydrocarbon molecule has a diameter of 0.38 nm, and so the mesopores and macropores are at least five times larger than the hydrocarbons. However, branched hydrocarbons with a diameter of 0.55 nm may be slowed down in the smallest mesopores. So depending on which type of reaction has to be carried out, a different mesopore size may be preferred.

Just making the pore size as large as possible, however, is not the only consideration when optimizing zeolite catalyst activity. A mesoporous matrix has more pores per volume than a macroporous matrix, which results in more entrances to the zeolite crystals – the sites where the reactions take place. Moreover, a macroporous matrix is not as mechanically robust as a mesoporous matrix. This can lead to breakdown of the catalyst to dust in commercial reactors, where the weight of the catalyst bed exerts high forces at the bottom of the bed. These arguments demonstrate the need for a method that allows fine-tuning of the pore architecture in the matrix and limitation of the zeolite crystal size, preferably all in one step.

Approach

The phenomenon of slow transport of reactants and products through the catalyst as described above was observed in various tests at our laboratory in Bloomfield. The tests showed that significant performance enhancement could be obtained by decreasing catalyst particle sizes from, for example, three millimeters to one millimeter. Reducing particle diameters creates more direct entrances to the catalyst and reduces the distance molecules have to travel through the pores of the catalyst particles to reach the sites where they are converted. Based on these results, it was concluded that the slow rate of transport of reactants and products through the matrix and in the zeolite crystals limited the activity of commercial zeolite catalysts. An experimental program was set up to develop a zeolite synthesis process that would provide a zeolite catalyst with ultra-small crystals and a high meso- and macropore volume; in other words, controlled pore size. This required a change from the normal way of thinking that had set the rules and guidelines of conventional synthesis.

In conventional zeolite synthesis methods, all building blocks of the zeolite structure are completely dissolved in water: silicon and aluminum sources, and cations. The cations are potassium or sodium or, in some cases, large organic molecules that act as a template around which the structure is formed. These organic molecules are the most expensive components for building the zeolite structure. The solution is transferred to a pressure reactor, where the mixture is heated at 80-200°C for 12 hours to 12 days. At temperatures close to or above the boiling point of water, vapor pressure builds up in the vessel. Specific concentrations, temperatures and times are chosen for each zeolite type. After crystallization of the zeolite is completed, the crystals, which are typically between 0.1 and 10 μm in size, are separated from the liquid by filtration or centrifugation. This solid/liquid separation process step is slow and expensive. If necessary, the crystals are heated in air to remove the organic template molecules. If the ultimate goal is to make a zeolite catalyst, the crystals are mixed with an aqueous ammonium solution to exchange the cations in the zeolite. Next, they are heated to obtain the active proton form. At this point of the production process, the zeolite product is still a fine dust and as such, is not suitable for use in commercial reactors. The powder has to be shaped into a form that allows easy handling and reactor operation at reasonable pressure drops. For this reason, the zeolite crystals are embedded in a porous matrix of alumina or silica-alumina.

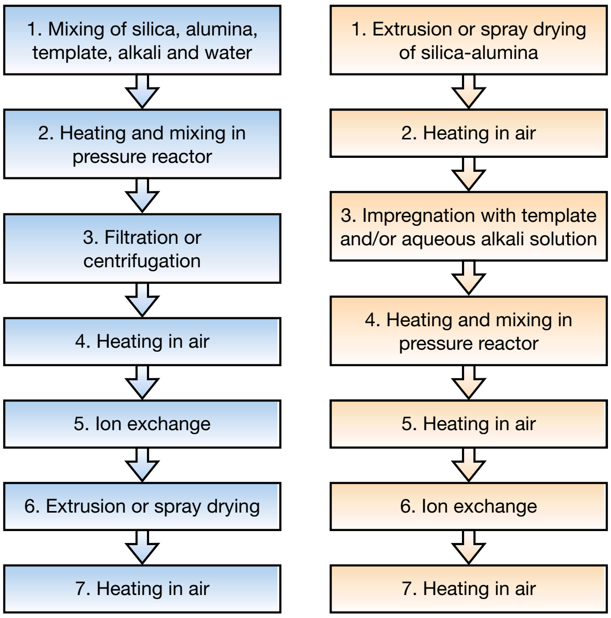
One method of shaping is spray drying, a process that is also used for the production of milk powder. Spray drying produces particles that are smaller than 200 μm. In most cases, however, catalyst shaping is done in a so-called extrusion process, similar to the production of spaghetti. The powder is mixed with water and the matrix component to form a paste and then passed through the extruder, which forms particles of 1 mm and larger. Due to differences in rheological properties, the extrusion of zeolites is more difficult and more limited than extrusion of silica, silica-alumina or alumina. Some material loss takes place, which is most costly when extruding a zeolite product. Due to the limitations of the extrusion and spray drying processes, the size of the meso- and macropores in the matrix cannot be controlled effectively.

ABB's novel zeolite synthesis technique

ABB has developed a novel synthesis method that is faster, uses raw materials more efficiently, reduces crystal sizes and offers pore size control. In contrast with conventional techniques, it is carried out in the absence of an external liquid. In particular, the method uses mesoporous precursor particles that are converted to catalyst particles with the same morphology as the precursor particles. All liquids that are used in this synthesis are contained within the pores of the solid, so that both the synthesis mixture and the products seem to be and have the flow behavior of dry solids. The synthesis mixture consists of mesoporous silica-alumina particles that are filled (impregnated) with liquid. During the transformation process, zeolite crystals are formed within the particles. Ideally, products from the novel zeolite synthesis have the morphology of the starting material. At the end of the synthesis, the impregnating liquid will still only be present in the pore volume of the particles, and thus the product can be collected as a powder. 2 shows the order of the process steps for the conventional zeolite synthesis and for the novel ABB synthesis technique.

The first step of the synthesis process is the key to success. Here the foundations of the final zeolite structure are set into place. The distribution of the silicon and aluminium needs to be homogeneous; any deviations from the required distribution lead to formation of unwanted zeolite phases or non-crystalline parts in the product. The starting particle needs to have the right pore size, since this determines the pore size that ultimately gives access to the zeolite crystals. Furthermore, the pore volume of the starting particle must allow sufficient liquid content for zeolite synthesis to occur. For most of the initial experiments, spray-dried 50 μm particles with mesopores of 20 nm were used. In a later phase of the development, commercial millimeter-size particles in the shape of cylinders and spheres were used successfully. The shaped particles are heated in air to release water and additives from the pores and prepare the material for the next impregnation step.

In the third process step, impregnation with the aqueous template or NaOH solution takes place by slow addition under stirring. To prevent breakdown of the particles in the next step, this impregnation was never carried out beyond the incipient wetness point of the alumino-silicate particles. This is the point at which the pores are completely filled with the liquid.



2 Steps in the production of zeolite catalyst particles with the conventional procedure (left) and the novel ABB method (right)

3 Equipment at ABB Corporate Research in Heidelberg for scale-up of the novel zeolite synthesis method at kilogram level

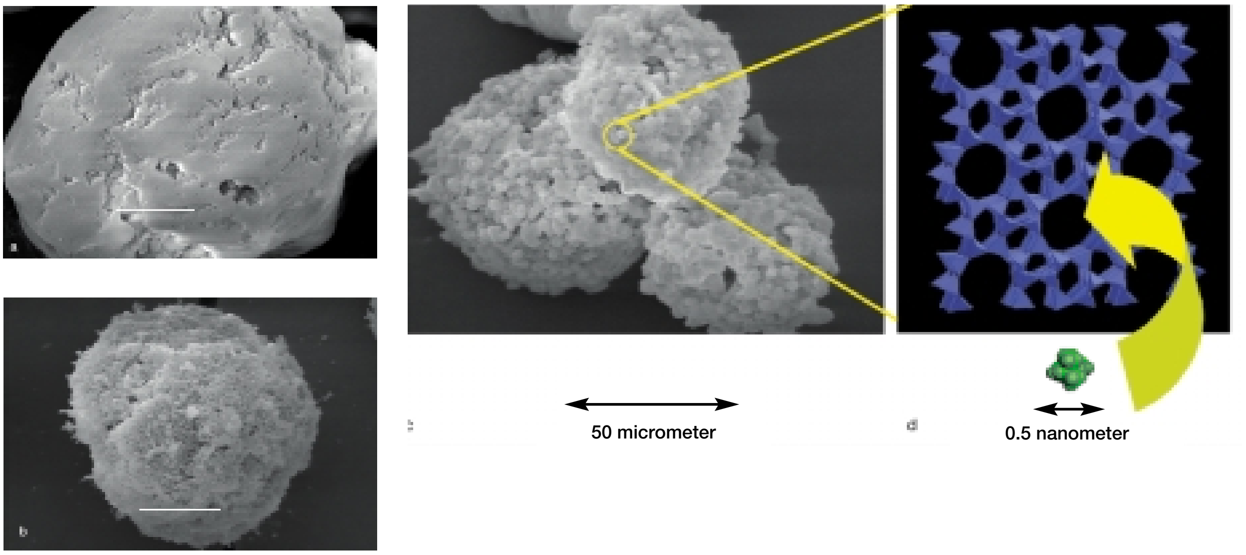
In the fourth process step, the final conversion of the ingredients to the zeolite takes place. This is a critical step in the synthesis procedure. Inhomogeneous heating of the mixture can lead to incomplete transformation, partial degradation of the particles and formation of more than one zeolite phase. Heat transfer from the reactor wall to the mixture is smaller than in normal liquid-phase zeolite synthesis because the synthesis mixture contains a large volume of solids with much lower heat conductivity than liquids. Constant agitation of the powder is imperative in order to obtain a uniform temperature throughout the autoclave. 3 shows the equipment that was used at the Corporate Research Center in Heidelberg, Germany, to make kilograms of zeolite product.

In contrast to conventional synthesis methods, the zeolite product is collected from the reactor without filtration. The geometrical features of the starting material – spray dried particles and extrudates – are maintained, and thus extrusion of the zeolite product is not necessary. This eliminates zeolite losses during extrusion and possible chemical changes in the zeolite induced by the extrusion process. Because extrusion of, for example, silica-alumina is easier than extrusion of zeolites, this technology enables the fabrication of zeolite catalyst particle sizes and shapes that could not be obtained previously. Treatment of the zeolite product to obtain the acid form (steps 5-7) is the same as in the conventional process.

Product features

The novel procedure has been demonstrated for the synthesis of zeolite catalysts and zeolite adsorbents that account for approximately 90% of the zeolite world market: beta, ZSM-5, mordenite X, Y, and A. 4a to 4c show the morphology of a typical 50 µm spray dried particle and some of the zeolite products obtained from this starting material. 4c also indicates a schematic enlargement of one of the zeolite crystals, pointing out the scale of the catalyst particles and the zeolite pores. The transformation of the spray dried particles and the 2.5 mm extrudates is carried out while maintaining the morphology of the starting particles. Transformation of the silica and alumina to zeolite can reach up to an estimated 95%. The transformation process can also be stopped at any given time to yield partially converted products. The novel synthesis procedure requires stoichiometric amounts or only a small excess of the expensive template molecules. The utilization of the template is generally between 75 and 100%, which is higher than for the conventional synthesis methods.

The quality of the zeolite product, expressed as crystallinity (the degree of ordering), is equal to or better than the quality of commercial zeolite powders. Transmission Electron Microscopy (TEM) and Scanning Electron Microscopy (SEM) indicate that the crystallite sizes of the mordenite, ZSM-5, Y and A products from the novel synthesis procedure are significantly smaller than the crystallite sizes in the commercial products. Typically, crystal sizes of these products are a factor of 3-10 smaller than those from commercial synthesis methods. Smaller crystallites are formed because the concentration of silica, alumina and template in the liquid



4 Morphology of a typical 50-µm spray-dried particle and some of the zeolite products obtained from it

a *Silica-alumina starting material (bar indicates 10 µm)*

b *Sphere after conversion to zeolite beta (bar indicates 20 µm)*

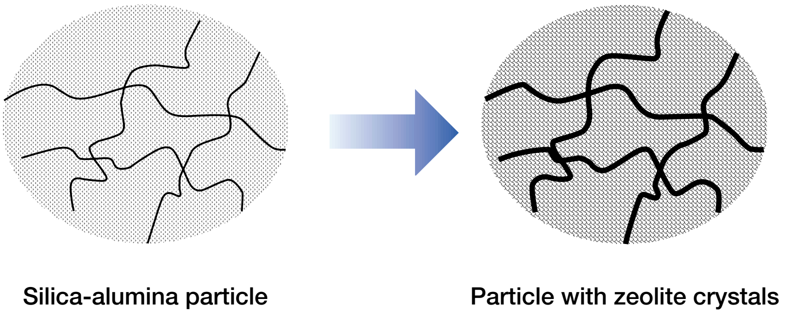
c *Particles after conversion to ZSM-5*

d *Schematic enlargement of a crystal, going from 50 µm to 0.5 nm, showing molecular scale of structure*

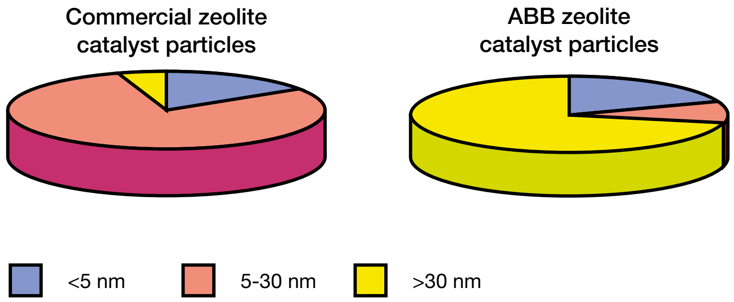
phase in the novel ABB procedure is higher than in conventional synthesis. In conventional syntheses, excess water is used to ensure good solution and molecular mixing of the silica and alumina building blocks. In the ABB procedure, the liquid phase is saturated during most of the zeolite crystallization period, which results in a very high rate of crystal formation. Moreover, as a result of the high concentrations the crystal growth rate increases dramatically, reducing the average synthesis time by a factor of two to three.

The total pore volume that is formed by the micro-, meso- and macropores of the starting particle is maintained because the particle shape and size of the starting material are maintained upon conversion. The pore size, however, changes as a result of the conversion to zeolites (see 5 and 6). In the spray-dried particles and the extrudates the pore sizes become larger upon conversion. It was also demonstrated that the pore size in the final product is determined by the pore size of the starting material. During the transformation process, parts of the substrates are 'mobilized', which results in a concentration of silica and alumina at discrete points and an increase in the pore size.

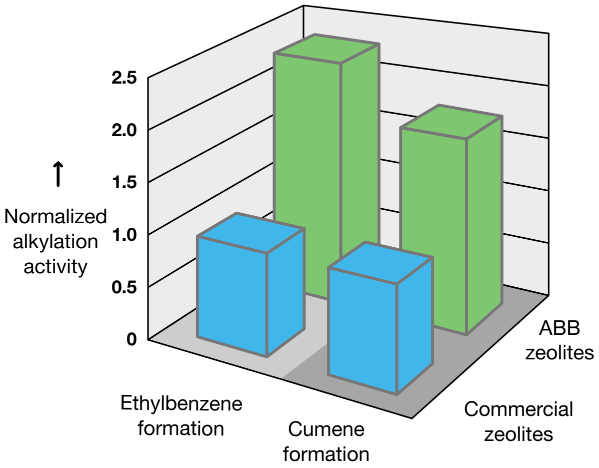
The starting point of this program was to obtain zeolite catalysts with improved particle porosity and reduced crystal size to improve catalytic performance. One of the product types, zeolite beta, was tested extensively for its activity in the alkylation of benzene to ethylbenzene and cumene. The activity was compared with the activity of zeolite beta catalysts used in commercial units. All samples were sieved to one particular size range so that the effect of particle size on activity could be disregarded. 7 shows the typical alkylation activity (per gram of catalyst) of ABB zeolite samples and commercial



5 Schematic representation of the novel zeolite synthesis procedure. Mesoporous silica-alumina particles are converted to zeolite catalysts with the same particle morphology. The mesopore size in the catalyst particles (black curved lines) increases upon conversion to zeolite, while the bulk of the material is converted from a non-porous silica-alumina to a microporous zeolite.



6 Pore size distribution in commercial and ABB zeolite catalyst particles



7 Normalized activity per gram of catalyst for ABB zeolites and commercial zeolites in the alkylation of benzene to ethylebenzene and cumene

catalysts. The samples from the novel procedure showed significantly higher performance than the commercial samples. The demonstrated success in the benzene alkylation reactions may only be 'the tip of the iceberg'. According to the principle of improved molecular transport, many other reactions may be caused to proceed at a higher rate by the use of these novel products. Several zeolite-manufacturing companies have shown interest in this proprietary ABB technology [3] and the zeolites that it produces. Scale-up has recently been achieved at ABB's Research Center in Heidelberg. These facilities now produce kilogram quantities of zeolite samples for testing in catalysis, adsorption and separation by interested companies.

Summary

ABB has invented and patented a novel technology for the production of zeolite catalysts and adsorbents. Advantages of this synthesis method over conventional zeolite synthesis methods are:

- Reduction of the total synthesis time per batch
- High utilization of the zeolite building blocks and the organic template
- Elimination of the expensive filtration step to collect zeolite product
- Replacement of zeolite extrusion by silica-alumina extrusion, so a less costly material is lost

The method offers a route to zeolite catalyst particles with specific product features, such as:

- High product crystallinity
- Small crystal sizes
- Tunable porosity

Superior performance of one particular zeolite product was demonstrated in the alkylation of aromatics. The combined features of the novel products is expected to lead to faster molecular transport in the zeolite catalyst particles, and thus potentially to superior performance in many other applications.

Authors

Nelleke van der Puil
Frits Dautzenberg
ABB Lummus Global
Technology Development Center
1515 Broad Street
Bloomfield NJ 07003, USA
nelleke.van_der_puil@us.abb.com
f.m.dautzenberg@us.abb.com

Jan Henk Koegler
ABB Research Center
Speyerer Strasse 4
D-69115 Heidelberg
Germany
jan.koegler@de.abb.com

References

[1] **E.M. Flanigen**: Zeolites and Molecular Sieves – A Historical Perspective. In 'Introduction to Zeolite Science and Practice' by H. van Bekkum, E.M. Flanigen and J.C. Jansen, Elsevier, Amsterdam, 1991.

[2] **M.M.J. Treacy**, **J.B. Higgins**, **R. von Ballmoos**: Collection of Simulated XRD Powder Patterns for Zeolites. Elsevier, Amsterdam,1996.

[3] **L.L. Murrell**, **R.A Overbeek**, **Y.F. Chang**, **N. van der Puil**, **C.Y Yeh**: Method for Making Molecular Sieves and Novel Molecular Sieve Compositions. US Patent no 6,004,527, 1999.