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Zeolites and catalysis

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Abstract

This review covers the fundamentals of zeolite materials science and their application as catalysts. After a brief introduction into their structures, the most important parameters are discussed which allow the preparation of an almost infinite variety of zeolitic materials tailored for a given catalytic application. Zeolites are solid acids, and the chemical nature, the density, strength and location of the acid sites in zeolites are discussed. Shape-selective catalysis, which is a unique feature of zeolites, is briefly addressed. © 2000 Elsevier Science B.V. All rights reserved.

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1. Introduction

Zeolites occur in nature and have been known for almost 250 years as aluminosilicate minerals. Examples are faujasite, mordenite, offretite, ferrierite, erionite and chabazite. Today, these and other zeolite structures are of great interest in catalysis, yet their naturally occurring forms are of limited value, because (i) they almost always contain undesired impurity phases, (ii) their chemical composition varies from one deposit to another and even from one stratum to another in the same deposit, and (iii) nature did not optimize their properties for catalytic applications.

It was only with the advent of synthetic zeolites from ca. 1948 to 1955 (thanks, mostly, to the pioneering work of Barrer and Milton) that this class of porous materials began to play a role in catalysis. A landmark event was the introduction of synthetic faujasites (zeolites X and Y) on an industrial scale in fluid catalytic cracking (FCC) of heavy petroleum distillates in 1962, one of the most important chemical processes worldwide. The new zeolitic catalysts were not only orders of magnitude more active than the previously used amorphous silica–alumina catalysts (which enabled drastic process engineering improvements [1]), but they also brought about a significant increase in the yield of gasoline, the most valuable product from FCC plants. It can be estimated [1,2] that this yield enhancement alone resulted in an added value in the order of at least several billion US dollars per year. It has further been estimated [3] that, as a whole, the cost of petroleum refining worldwide would be higher by at least 10 billion US dollars per year, if zeolite catalysts were not available today.

In the period after 1962, zeolite catalysts rapidly conquered additional processes in the fields of

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petroleum refining and basic petrochemistry. The most important of these processes are hydrocracking of heavy petroleum distillates [4], octane number enhancement of light gasoline by isomerization [5], the synthesis of ethylbenzene (the precursor of styrene and polystyrene) from benzene and ethene after the Mobil–Badger process [6], the disproportionation of toluene into benzene and xylenes [7] and the isomerization of xylenes (to produce *para*-xylene, the precursor chemical for terephthalic acid). In the manufacture of fine chemicals, the application of zeolite catalysts is still limited, even though their potential is considered to be very high in this area as well [8,9]. Altogether, catalysis is the single most important application of zeolites in terms of financial market size (not in terms of tonnage) with an estimated market volume around 1 billion US dollars per year [3].

This review will cover the basic principles of zeolite chemistry and catalysis. After a brief treatment of their structures, those properties of zeolites will be addressed which are of utmost importance in their use as catalysts, viz. surface acidity and shape selectivity.

2. Structures and definitions

The elementary building units of zeolites are SiO_4 and AlO_4 tetrahedra. Adjacent tetrahedra are linked at their corners via a common oxygen atom, and this results in an inorganic macromolecule with a structurally distinct three-dimensional framework. It is evident from this building principle that the net formulae of the tetrahedra are SiO_2 and AlO_2^-, i.e. one negative charge resides at each tetrahedron in the framework which has aluminum in its center. The framework of a zeolite contains channels, channel intersections and/or cages with dimensions from ca. 0.2 to 1 nm. Inside these voids are water molecules and small cations which compensate the negative framework charge. The chemical composition of a zeolite can hence be represented by a formula of the type

$$A^{m+}_{y/m}[(SiO_2)_x \cdot (AlO_2^-)_y] \cdot zH_2O \qquad (1)$$

where A is a cation with the charge m, $(x+y)$ is the number of tetrahedra per crystallographic unit cell and x/y is the so-called framework silicon/aluminum ratio n_{Si}/n_{Al} (or simply Si/Al). Löwenstein's rule [10] precludes that two contiguous tetrahedra contain aluminum on tetrahedral positions, i.e. Al–O–Al linkages are forbidden, or $n_{Si}/n_{Al} \geq 1$. Silicon and aluminum in aluminosilicate zeolites are referred to as the T-atoms.

Fig. 1 shows the structures of four selected zeolites along with their respective void systems and pore dimensions. In these commonly used representations, the T-atoms are located at the vertices, and the lines connecting them stand for T–O–T bonds. For example, if 24 tetrahedra are linked together as shown in the top line of Fig. 1, the cubo-octahedron, also referred to as a sodalite unit or β-cage, results. It is an important secondary building unit from which various zeolite structures derive. If sodalite units are connected via their hexagonal faces as shown in Fig. 1, the structure of the mineral faujasite results. It is identical with the structures of the synthetic zeolites X ($1 \leq n_{Si}/n_{Al} \leq 1.5$) and Y ($n_{Si}/n_{Al} > 1.5$). Zeolite Y is of utmost importance in heterogeneous catalysis, for example it is the active component in catalysts for fluid catalytic cracking [1,2]. Its pore system is relatively spacious and consists of spherical cages, referred to as supercages, with a diameter of 1.3 nm connected tetrahedrally with four neighboring cages through windows with a diameter of 0.74 nm formed by 12 TO_4-tetrahedra. Zeolite Y is therefore classified to possess a three-dimensional, 12-membered-ring pore system.

An example of a zeolite with unidimensional, 12-membered-ring pores is zeolite ZSM-12 (Fig. 1, line 2). Its pores are slightly elliptical with dimensions of 0.57×0.61 nm. Zeolite ZSM-5 (Fig. 1, line 3) and its all-silica analogue silicalite-1 ($n_{Si}/n_{Al} = \infty$) are built from the pentasil unit. They contain intersecting systems of ten-membered-ring pores, one being straight and one sinusoidal. ZSM-5 is another example of a zeolite which has gained huge importance in heterogeneous catalysis. It is used industrially in the synthesis of ethylbenzene, the isomerization of xylenes and the disproportionation of toluene, and it is often looked upon as the prototype of shape-selective catalysts (vide infra). Several zeolites with unidimensional, ten-membered-ring pores exist as well, one example being Theta-1 which is isostruc-

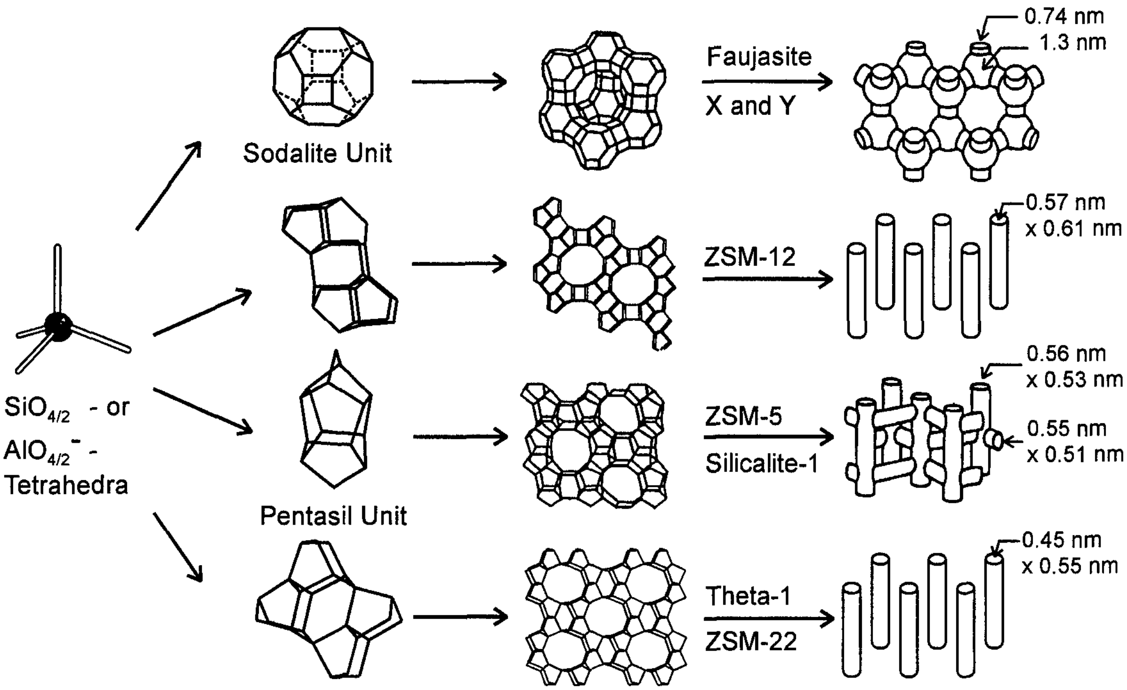

Fig. 1. Structures of four selected zeolites (from top to bottom: faujasite or zeolites X, Y; zeolite ZSM-12; zeolite ZSM-5 or silicalite-1; zeolite Theta-1 or ZSM-22) and their micropore systems and dimensions.

tural to zeolite ZSM-22 (Fig. 1, bottom line). An assortment of zeolite catalysts as shown in Fig. 1 is often a good starting point for a coarse investigation of the influence of the pore width and/or dimensionality on the selectivity of the reaction to be studied.

Among the unique features of zeolites compared to more conventional solid catalysts or catalyst supports are (i) their strictly uniform pore diameters and (ii) pore widths in the order of molecular dimensions (Fig. 2). Bearing in mind the pertinent IUPAC classification [11] for

micropores: $2.0\ \text{nm} \geq d_p$,

mesopores: $2.0\ \text{nm} < d_p \leq 50\ \text{nm}$ and

macropores: $d_p > 50\ \text{nm}$

with d_p being the pore diameter, zeolites are typical microporous materials. More conventional porous solids have their range of pore diameters from ca. 10 nm onwards (cf. Fig. 2), and for some time there was a gap in the lower mesopore range.

This gap was filled recently with the discovery of mesoporous materials of the M41S family [12], the most prominent and most extensively investigated member of this family being MCM-41. MCM-41 is a hexagonal material containing a regular array of mesopores with uniform diameter. By proper synthesis procedures, the pore diameter can be varied from ca. 2 to 10 nm. The M41S materials are often referred to as ‘mesoporous zeolites’. Indeed, MCM-41 resembles a zeolite with respect to its regular system of pores with their uniform width. There is, however, one significant difference, namely the noncrystallinity of the silica or silica–alumina pore walls in MCM-41.

The most appropriate definition of the term *zeolite* is a matter of ongoing debate. Mineralogists tend to restrict it to aluminosilicates according to Eq. (1). Zeolites are then crystalline aluminosilicates with a framework forming regular channels with a diameter of up to ca. 1 nm. These channels contain cations (frequently Na^+ ions), which compensate the nega-

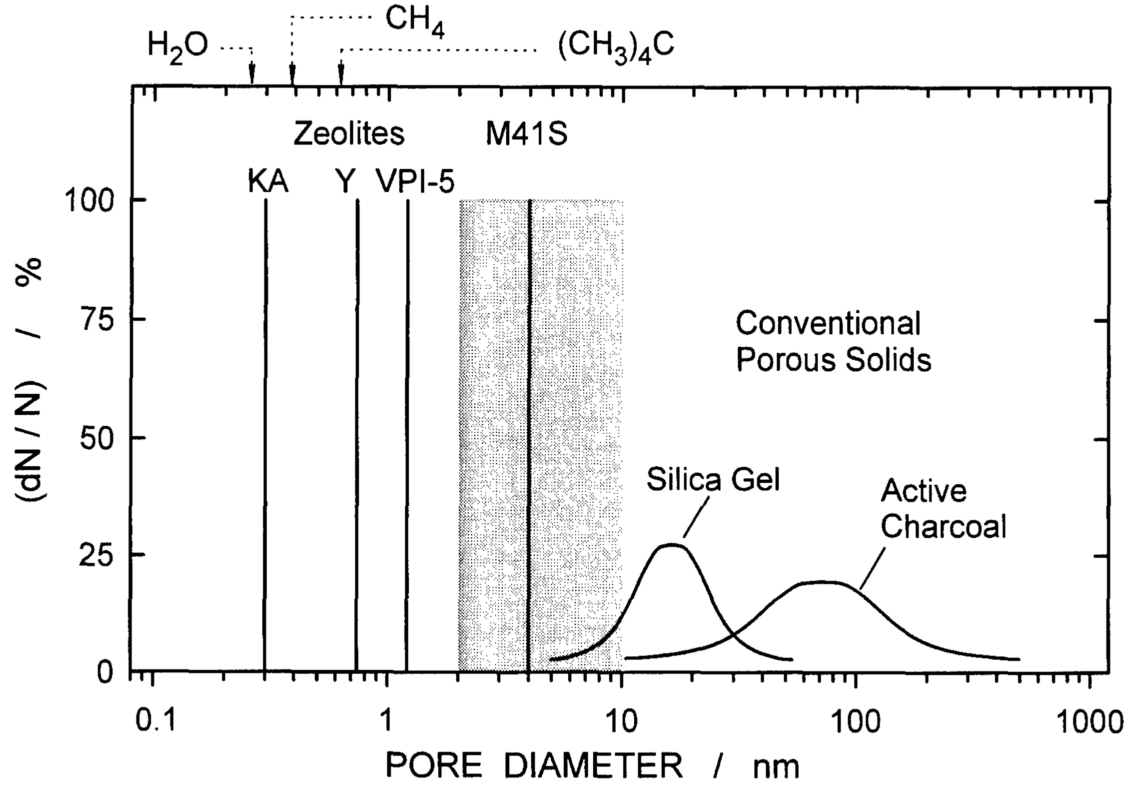

Fig. 2. Typical pore diameter distributions of porous solids (KA is the K^+ form of zeolite A; VPI-5 is a microporous aluminophosphate with 18-membered-ring pores; for the description of M41S materials see Section 2). For comparison, the kinetic diameters of water, methane and neopentane are also indicated.

tive framework charge and are very mobile, and water which desorbs upon heating without destruction of the crystalline structure.

Liebau et al. [13,14] suggested the classification of the materials in the large group of tectosilicates according to their chemical composition (aluminosilicates: *tectolites*; SiO_2: *tectosils*) and their framework or tetrahedral density ρ_T defined as the number of TO_4 tetrahedra n_T per nm^3. Tectosilicates with $\rho_T \geq 21$ n_T/nm^3 are referred to as *dense* and divided into *pyknolites* (aluminosilicates, e.g. nepheline, cordierite or feldspars) and *pyknosils* (SiO_2, e.g. quartz or cristobalite). These materials lack porosity and are, hence, of no interest by themselves as catalysts (though sometimes as catalyst carriers). Tectosilicates with $\rho_T < 21$ n_T/nm^3 are called *porous* and divided into *porolites* (aluminosilicates) and *porosils* (SiO_2). Sub-classes of the porolites are *clathralites* (e.g. sodalite or ZSM-39) and *zeolites*. Clathralites possess voids with windows (usually formed by six TO_4 tetrahedra) which are too small to let the void-filling guests pass. Such tectosilicates have the characteristics of clathrates and are not of interest in catalysis. In zeolites, by contrast, the cavities possess windows large enough for guest molecules to diffuse through. In much the same way, sub-classes of porosils are *clathrasils* (e.g. silica–sodalite or melanophlogite) and *zeosils* (e.g. silicalite-1 or silica-ZSM-22). Liebau's nomenclature, though very straightforward and systematic, has unfortunately found limited acceptance, though its salient terms are being used occasionally in the literature [15].

Today, a broad variety of zeolite-like microporous materials are known with T-atoms other than silicon and aluminum. For these materials, Dyer proposed the term *zeotypes* [16]. The best known examples are microporous aluminophosphates ($AlPO_4s$) and materials derived from them by incorporation of T-atoms other than aluminum and phosphorus [17,18]. All these and related microporous materials with still other T-atoms like titanium, vanadium, cobalt, etc. are of considerable interest in catalysis and routinely dealt with at the International Zeolite Conferences. The terms *zeolites*, *microporous materials* and *molecular sieves* are therefore often used as synonyms indicating that the regular array of micropores with well-defined dimensions is the unifying principle which renders this wealth of materials attractive for catalysis (and other applications).

3. Broad variety of zeolitic materials available

3.1. Structure and pore size

Four selected zeolite structures were shown in Fig. 1, but many more are available today. A huge number of zeolitic materials has been described in the literature, and a great deal of these in the patent literature. It is sometimes difficult, especially for researchers whose prime interest lies in catalysis, to find out whether such reported materials possess truly new structures or whether they represent variants of structures already known. In this context, the work of the Structure Commission of the International Zeolite Association (IZA) has been most valuable. Composed of 16 experienced crystallographers, the Commission regularly scrutinizes proposed zeolite structures. Once a structure has been approved by the Commission, it is assigned a three-letter code (e.g. FAU for faujasite and zeolites X and Y; MTW for zeolite ZSM-12; MFI for zeolite ZSM-5 and its zeosil analogue silicalite-1; TON for zeolites Theta-1 and ZSM-22 which are isostructural) and included in the ‘Atlas of Zeolite Structure Types’. Its latest edition appeared in 1996 [19] and embraces 98 structures. An additional 28 structures have since been published on the world wide web.

At this time (December 1999), there is hence a total of 126 approved zeolites structures. In Fig. 3, their range of crystallographic pore diameters is

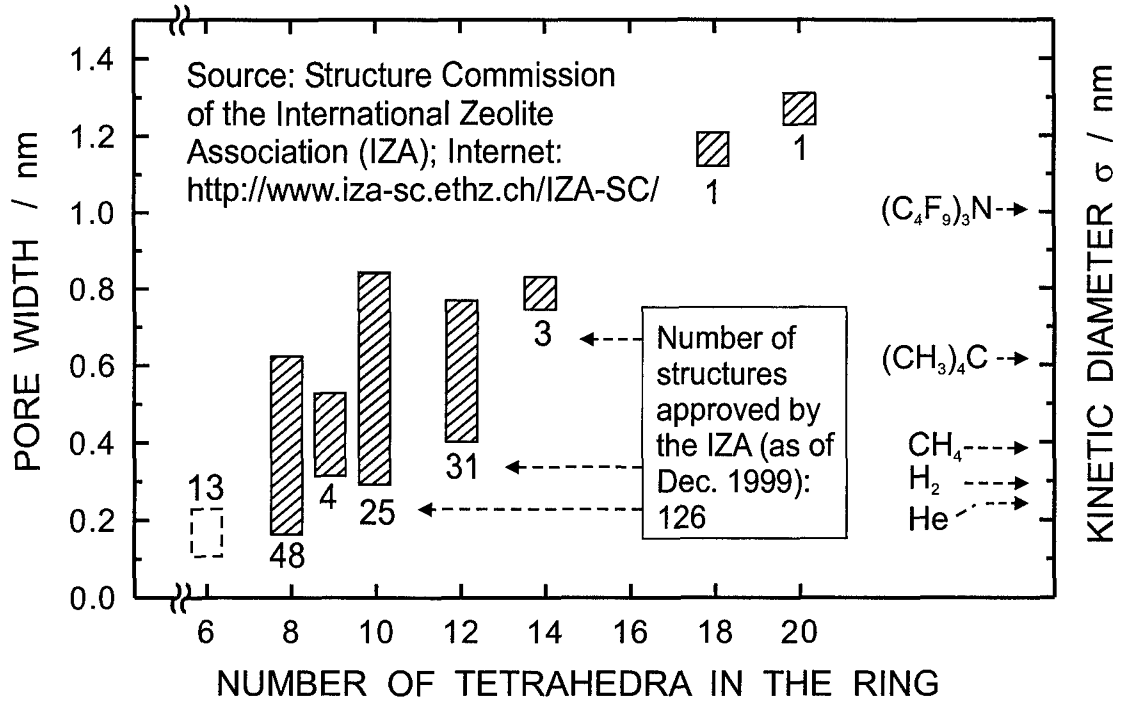

Fig. 3. Range of crystallographic pore diameters of zeolites approved by the Structure Commission of the International Zeolite Association (IZA). Sources: Ref. [19] and internet homepage of the IZA Structure Commission.

plotted versus the number of TO_4-tetrahedra circumscribing their pores. The largest, i.e. catalytically most relevant pores were chosen for those zeolites which possess more than one pore system. The kinetic diameters (σ in the Lennard–Jones model for intermolecular interactions) for a few selected molecules are also given in Fig. 3 for comparison. It is seen that there are 13 structurally different clathralites/clathrasils with six-membered-ring pores. Such pores are generally too narrow (around 0.2 nm) to admit the molecules involved in catalytic reactions. The remaining 113 zeolites span a range of pore widths which coincides with the range of dimensions of a very large number of molecules. It is furthermore seen from Fig. 3 that zeolites with eight-, ten- and 12-membered-ring pores for which, respectively, the terms small-pore, medium-pore and large-pore zeolites are customary, strongly predominate with a total of 104 structures, whereas the super-large-pore materials with pores formed by more than 12 TO_4-tetrahedra and materials with pores formed by an odd number of TO_4-tetrahedra are still scant.

The potential of zeolites with nine-membered-ring pores has so far hardly been explored. Zeolites with eight-membered-ring pores are good catalysts for a limited number of reactions involving small reactant and product molecules. Examples are the manufacture of mono- and dimethylamine from methanol and ammonia or the conversion of methanol to small olefins (MTO). For the majority of catalytic applications, medium- or large-pore zeolites will usually be preferred.

Fine-tuning and tailoring of the pore size of a given zeolite can be achieved by various post-synthesis modification techniques for which the generic term 'pore size engineering' has been coined [20]. Among these techniques are ion exchange and chemical vapor deposition (CVD). A frequently used class of CVD precursors are silanes and organosilanes, such as tetramethoxysilane or tetraethoxysilane.

3.2. Chemical composition

Many aluminosilicate zeolites can be synthesized over a range of aluminum contents, for example zeolite ZSM-5 from $n_{Si}/n_{Al} \approx 10$ to ∞. In addition, various techniques for the post-synthesis dealumination of the framework have been developed which can be classified into thermal treatments, hydrothermal treatments, extraction of framework aluminum with acid and replacement of framework aluminum with silicon by reaction with silicon halides or hexafluorosilicates [21]. Conversely, an insertion of aluminum into the zeolite framework can be achieved as well [21]. Among the properties which are affected by the framework aluminum content are the density of negative framework charges, the cation-exchange capacity, the density of Brønsted acid sites, their strength, the thermal stability, the hydrophilic or hydrophobic surface properties [22] and the unit cell dimensions.

As already mentioned, a number of elements other than silicon or aluminum can occur as T-atoms. Relevant to catalysis are silicoaluminophosphates, in part because some of these materials possess structures which do not exist for aluminosilicates, and in part because their acid strength is lower than the one of aluminosilicate zeolites. Materials containing titanium, vanadium, iron and other transition metals in the framework have recently attracted much interest as catalysts for selective oxidations [23]. The most prominent example is titanium silicalite-1 (TS-1, MFI structure) which is used on an industrial scale for the production of hydroquinone and catechol from phenol and hydrogen peroxide [24].

3.3. Ion exchange

With their negatively charged porous framework and the small and mobile cations sitting in the pores, zeolites are typical ion exchangers. In fact, zeolites are widely used as builders in laundry detergents where their role is to take up calcium and magnesium ions in exchange for sodium ions, thereby softening the washing water. Obviously, an as high as possible cation exchange capacity and, hence, the highest possible aluminum content in the framework ($n_{Si}/n_{Al} = 1$) are desired for this application. This is the domain of zeolite A, and as a whole, the use of zeolites as ion exchangers in detergents represents their largest market in terms of tonnage (not in terms of financial turnover) with a worldwide production rate close to 1 million t/annum.

In the manufacture of zeolite catalysts, ion exchange plays an outstanding role as well. For many catalytic applications, a Brønsted acid form of a zeolite is required. Brønsted acid sites in zeolites can be readily generated by introducing ammonium ions followed by a heat treatment or by introducing multivalent metal cations, typically cations of the rare-earths, again followed by heat treatment (vide infra). In processes which work under hydrogen pressure, such as hydrocracking of heavy petroleum distillates or the isomerization of light gasoline, bifunctional catalysts are needed which contain both Brønsted acid sites and a component which activates hydrogen, typically a noble metal like palladium or platinum. These noble metals can again be easily introduced into the zeolite pores by ion exchange with cationic forms of such metals, e.g. $[Pd(NH_3)_4]^{2+}$ or $[Pt(NH_3)_4]^{2+}$, followed by thermal removal of the ammine ligands. More recently, the use of metal-containing zeolite catalysts for the selective reduction of nitrogen oxides with light hydrocarbons, e.g. in exhaust gases from diesel engines, has become a topic of worldwide research [25,26]. Here again, ion exchange is almost always applied to incorporate the frequently studied metals like Cu, Co, Pt or Pd into the zeolite.

Ion exchange is a very simple technique: The zeolite is suspended in an aqueous solution of a soluble salt containing the desired cation, preferentially under conditions which favor mass transfer, i.e. at elevated temperatures (ca. 90°C) under stirring. While this procedure is very versatile, it has its limitations: Sometimes, the cation with its hydrate shell is too bulky to enter the zeolite pores, or the salt with the cation in the desired valence state is unstable or insoluble in water. In these and other instances, the desired form of the zeolite can often be made by solid-state ion exchange: The zeolite, typically in its H^+-form, and a compound containing the in-going cation, e.g. a halide, are intimately mixed, whereupon this physical mixture of solids is heated in an inert gas stream. An excellent review on solid-state ion exchange with zeolites and its variants, viz. contact-induced solid-state ion exchange, vapor phase-mediated ion exchange and reductive solid-state ion exchange has recently been published by Karge [27].

3.4. Crystal size

The size of zeolite crystals is often in the order of one to several micrometers. A typical example is depicted in Fig. 4a which shows tablets of zeolite ZSM-5 with dimensions of 1 to 3 μm. Some zeolites which are relevant to catalysis can, however, be synthesized in very small crystals with a size down to ca. 5 nm (such small crystals are X-ray-amorphous [28]) or in very large crystals up to ca. 100 μm or even 1 mm [29]. As an example, large crystals of zeolite ZSM-5 are shown in Fig. 4b. For catalytic applications, both a decreased and an increased crystal size can be desirable: Upon decreasing the crystal size, the diffusional paths of the reactant and product molecules inside the pores become shorter, and this can result in a reduction or elimination of undesired diffusional limitations of the reaction rate. However, while decreasing the crystal size, one must be careful, since below ca. 0.1 μm the external crystal surface begins to play a non-negligible role vis-à-vis the internal surface, and this is particularly undesirable if shape selectivity effects are to be exploited. Shape selectivity, which is a unique effect in zeolite catalysis, can only occur inside the channel and cage system (vide infra). Conversely, upon increasing the crystal size, the diffusional paths of the molecules inside the pores are lengthened, and this may, under certain circumstances, affect the selectivity in a desirable manner.

4. Acidity of zeolites

Among the most important properties of zeolites with respect to their use as catalysts is their surface acidity. To describe the acidity of zeolites in an adequate manner, it is mandatory to clearly distinguish between (i) the nature of the acid sites (i.e. Brønsted vs. Lewis acidity), (ii) the density or concentration of these sites, (iii) their strength or strength distribution and, last but not least, (iv) the precise location of the acid sites.

4.1. Nature of the acid sites

Both Brønsted and Lewis acid sites occur in zeolites. Brønsted acid sites are almost always generated by either of the procedures represented by Eqs. (2) and (3), where Z^- stands for the negatively charged framework:

$$NH_4^+ + Na^+Z^- \xrightarrow[-Na^+]{} NH_4^+Z^- \xrightarrow[-NH_3]{\approx 300-400°C} H^+Z^- \qquad (2)$$

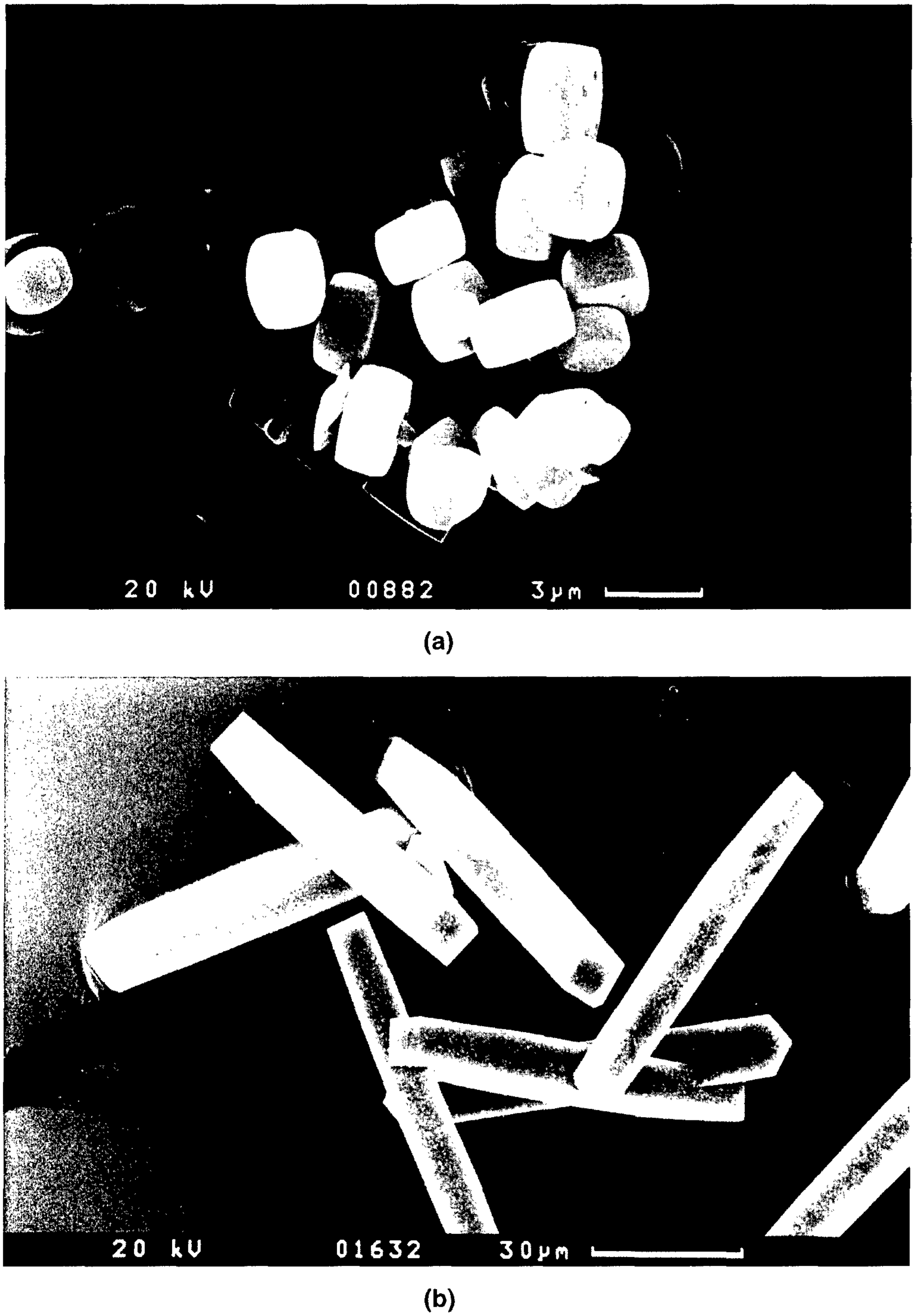

Fig. 4. Scanning electron micrographs showing crystals of zeolite ZSM-5. (a, top): Tablets of ca. 2×2 ×1 μm; (b, bottom): Bars of ca. 80×10×10 μm.

i.e. aqueous ion exchange with an ammonium salt followed by thermal decomposition of the ammonium ions inside the zeolite, or

$$[\mathrm{La(H_2O)}_n]^{3+} + 3\mathrm{Na^+Z^-} \xrightarrow[-3\,\mathrm{Na^+}]{} [\mathrm{La(H_2O)}_n]^{3+}(\mathrm{Z^-})_3 \xrightarrow[-(n-2)\,\mathrm{H_2O}]{\approx 300^\circ\mathrm{C}} [(\mathrm{LaOH})(\mathrm{H_2O})]^{2+}\mathrm{H^+}(\mathrm{Z^-})_3 \rightarrow [\mathrm{La(OH)_2}]^{+}(\mathrm{H^+})_2(\mathrm{Z^-})_3 \qquad (3)$$

i.e. aqueous ion exchange with the salt of a multivalent metal cation (often used are Mg^{2+}, Ca^{2+}, La^{3+} or mixed rare-earth cations) followed by thermal dehydration. The sequence of events in Eq. (3) is usually referred to as the Hirschler–Plank scheme: Upon removal of most of the water from the cation inside the zeolite pores, strong electrostatic fields build up, because the lanthanum ion has to neutralize three negative charges fixed in the framework at a significant distance from each other. Under the influence of these local electrostatic fields, remaining water molecules dissociate giving rise to a proton and an OH group which is non-acidic and bound to the metal cation. It is seen from Eq. (3) that a maximum of two Brønsted acid sites can be formed per La^{3+} ion introduced.

The direct ion exchange with mineral acids

$$\mathrm{H^+} + \mathrm{Na^+Z^-} \xrightarrow[-\mathrm{Na^+}]{} \mathrm{H^+Z^-} \qquad (4)$$

is generally less favored, because an exposure of zeolites to such acids often leads to undesired effects like framework dealumination or, in the case of aluminum-rich zeolites, to a complete framework collapse.

Finally, Brønsted sites inevitably form, when cations of metals nobler than hydrogen are reduced by molecular hydrogen:

$$[\mathrm{Pd(NH_3)_4}]^{2+} + 2\mathrm{Na^+Z^-} \xrightarrow[-2\,\mathrm{Na^+}]{} [\mathrm{Pd(NH_3)_4}]^{2+}(\mathrm{Z^-})_2 \xrightarrow[-4\,\mathrm{NH_3}]{\approx 300^\circ\mathrm{C}} \mathrm{Pd^{2+}}(\mathrm{Z^-})_2 \xrightarrow{+\mathrm{H_2}} \mathrm{Pd^0}(\mathrm{H^+})_2(\mathrm{Z^-})_2 \qquad (5)$$

Regardless of the method used for their generation [Eqs. (2)–(5)], the chemical nature of the Brønsted acid sites is the same, viz. bridging hydroxyl groups formed by the proton and a framework oxygen in an AlO_4 tetrahedron.

Upon severe heat treatment (≥500°C), the Brønsted acid sites are degraded ('dehydroxylation'), water is split off with the concomitant formation of Lewis acid sites. Their precise chemical nature is less clear. For some time, they were looked upon as tricoordinated aluminum and/or tricoordinated, positively charged silicon in the framework. Kühl, however, was able to demonstrate [30] that silicon in dehydroxylated zeolites remains tetracoordinated and much of the aluminum is converted to octahedral rather than trigonal coordination. This led Kühl to conclude that $[(\mathrm{AlO})^+]_n^{n+}$ units removed from the zeolite framework act as true Lewis sites.

The Brønsted OH groups can be directly detected by solid-state IR (Fig. 5a) and ^{1}H-NMR (Fig. 5b) spectroscopy. In the OH-stretching region of the IR spectrum, acid faujasites (see Fig. 1, top line, for their structure) show essentially two bands appearing at ca. 3550 cm^{-1} and 3640 cm^{-1}. These bands are, respectively, due to bridging OH groups in the small sodalite cages and in the large supercages. In line with this assignment, the band at 3640 cm^{-1} disappears upon adsorption of the base pyridine, whereas the band at 3550 cm^{-1} does not. Obviously, the pyridine molecule is too bulky to penetrate the small cages. This is an example of a molecular sieve effect. In the region of ring deformation vibrations, new bands appear after adsorption of pyridine. The band around 1540 cm^{-1} is due to pyridinium ions chemisorbed on Brønsted acid sites, whereas the band at 1455 cm^{-1} is indicative of pyridine on Lewis acid sites. Note that the small band at ca. 3740 cm^{-1} originates from terminal, non-acidic OH bands either at the external surface of the crystals or at amorphous inclusions. It should also be mentioned that, unlike faujasite, most high-silica zeolites such as HZSM-5 show a single band in the OH-stretching region which appears close to 3600 cm^{-1}.

The ^{1}H-NMR spectrum of acid faujasite (Fig. 5b) consists of an intense signal at 3 to 6 ppm. After deconvolution, the signals for bridging OH groups in the large and in the small cages appear at 3.9 and 4.8 ppm, respectively. The combined application of solid-state IR and NMR spectroscopy has significantly contributed to our understanding of zeolite acidity, especially in relation to catalytic activity. An

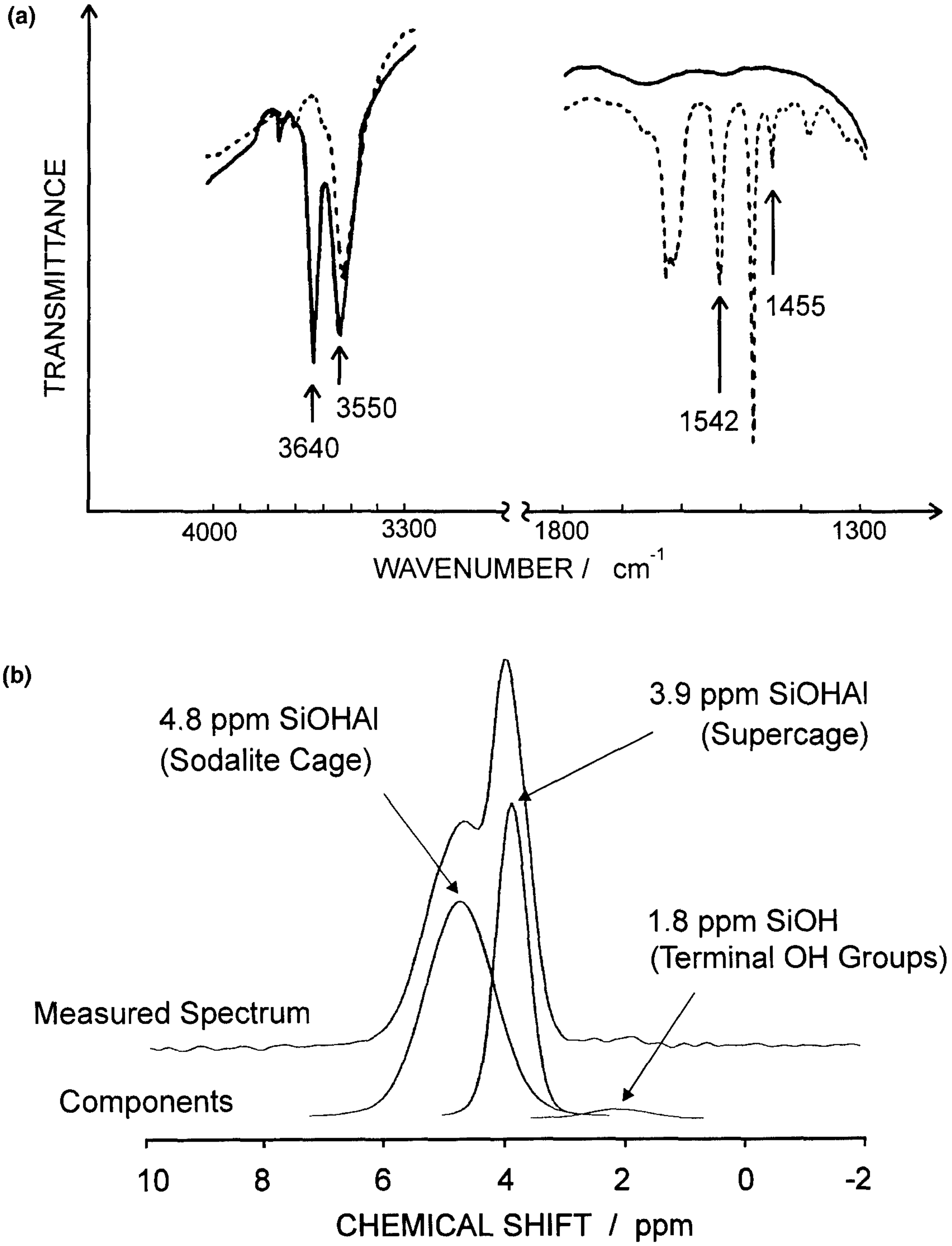

Fig. 5. (a, top): IR spectra of HY zeolite without (solid lines) and with (dotted lines) adsorbed pyridine; (b, bottom): ^{1}H-MAS-NMR spectrum of HY zeolite.

excellent account on solid-state IR and NMR spectroscopy and the information they furnish with respect to zeolite catalysis may be found in the recent literature [31].

It has been repeatedly found that the catalytic activity stems from the Brønsted rather than the Lewis acid sites. It is doubtful whether the Lewis sites play a role at all in acid-catalyzed reactions. It has been claimed [32] that, under certain circumstances, Lewis acid sites might enhance the strength of nearby Brønsted sites, thereby exerting an indirect influence on the catalytic activity.

4.2. Density and strength of acid sites

The density of Brønsted acid sites in a zeolite is obviously related to the framework aluminum content. Limiting cases are pure zeosils, which lack acidity, and aluminum-rich zeolites such as HY. Note that zeolite X which is even richer in aluminum is unstable in the H^+-form. The density of Brønsted sites can be measured by, e.g. ^{1}H-NMR spectroscopy or IR spectroscopy, either with or without adsorption of a base like pyridine, but the latter technique requires the knowledge of reliable extinction coefficients which are often difficult to find. Similarly, the density of Lewis acid sites is accessible through IR measurements using the 1455 cm^{-1} band after adsorption of pyridine (here again reliable extinction coefficients are needed). An alternative method is to measure the total number of acid sites by titration with a gaseous base like ammonia and to subtract the number of Brønsted acid sites which has to be determined separately.

Less readily obtained is the strength distribution of acid sites in zeolites. Calorimetric methods measuring the heat of adsorption of nitrogen bases probably give the most reliable results, but such experiments tend to be cumbersome and require very experienced experimentalists. Semi-quantitative results may be obtained by IR spectroscopy with bases like pyridine at a set of suitably selected temperatures. Temperature-programmed desorption of bases like ammonia or pyridine are most frequently employed, because the technique is simple and versatile. However, the results must be interpreted with care, since hindered diffusion of the desorbed base out of the pores and multiple adsorption/desorption may obscure the desired information.

All these techniques indicate that zeolites are significantly stronger acids than their forerunners in industrial catalysis, i.e. amorphous silica-aluminas, and it is in the first place this enhanced acid strength which made zeolites so valuable and successful in processes like catalytic cracking. The recently discovered mesoporous materials like MCM-41 do not possess the high acid strength of zeolites, and this is a major hurdle which, together with the relatively high cost of their manufacture, so far prevented them from being applied as catalysts in industrial processes.

It is well known and supported by quantum chemical calculations that, due to the higher electronegativity of silicon compared to aluminum, the strongest Brønsted acid sites in zeolites will occur on completely isolated AlO_4-tetrahedra, i.e. those which lack AlO_4-tetrahedra as next nearest neighbors. This is the reason why, upon dealumination of Y-zeolites with a typical n_{Si}/n_{Al} of 2.5, the catalytic activity generally *increases* up to $n_{Si}/n_{Al} \approx 10$. In this region, the gain in acid strength overcompensates the decrease in the density of Brønsted acid sites. From a certain n_{Si}/n_{Al} onwards (and with high-quality zeolite samples) the activity per acid site remains constant [32]. For a more detailed discussion of the important issue of zeolite acidity, the review by Rabo and Gajda [33] can be recommended.

4.3. Location of the acid sites

A complete description of zeolite acidity would include a detailed analysis of the location of the catalytically active sites. To what extent do these occur on the external surface of the crystals and inside the pores (only the internal surface can be expected to show shape selectivity, vide infra)? To what extent do the sites occur in large cavities, which are accessible for bulky reactant molecules, and in smaller cavities in which they are hidden for such molecules? Are the acid sites evenly distributed over the crystals, or are they concentrated in a shell near the external surface or, conversely, in the core of the crystals? More and more examples for surprising distributions of the location of acid sites are emerging in the literature. One example is the acid form of zeolite ferrierite which possesses both eight-membered-ring (dimensions: 0.35×0.48 nm) and ten-membered-ring (0.42×0.54 nm) pores. Interestingly, about three quarters of the Brønsted acid sites are located in the eight-membered-ring pores and hence inaccessible to many potential reactant molecules [34,35].

5. Shape-selective catalysis in zeolites

The fact that the pores of zeolites and molecules interacting with the surface of zeolites have dimensions in the same order of magnitude (cf. Figs. 2 and 3), leads to unique effects in catalysis for which the generic term shape-selective catalysis is in use today. Shape-selective catalysis encompasses all effects in which the selectivity of the heterogeneously catalyzed reaction depends unambiguously on the pore width or pore architecture of the microporous catalyst [36].

Numerous such effects are known today. Almost always, they can be classified into one of the following categories:

(i) *Reactant shape selectivity*: There are at least two reactants with differences in their molecular dimensions. If the diffusion of the bulkier reactant molecules inside the pores is hindered, the less bulky molecules will react preferentially. The limiting case is a complete size exclusion of one reactant which leaves the catalytic reactor unconverted.

(ii) *Product shape selectivity*: At least two products with differences in their molecular dimensions may form in parallel or consecutive reactions. If the diffusion of the bulkier product molecules inside the pores is hindered, the less bulky molecules will be formed preferentially. The limiting case is a complete suppression of the formation of the bulkier molecules.

(iii) *Restricted transition state shape selectivity*: Neither the reactant nor the product molecules experience a hindered diffusion. However, out of at least two (parallel or consecutive) reactions, one is going via a bulky transition state or intermediate which cannot be accommodated inside the zeolite pores. In favorable cases, this reaction is entirely suppressed. The chances for achieving restricted transition state shape selectivity in a suitably selected zeolite are usually very good, if the same reactant can undergo a monomolecular and a bimolecular reaction.

Note that cases (i) and (ii) are identical in their nature and have their origin in mass transfer effects. If desired, these effects can be amplified (or weakened) by using larger (or smaller) crystals of the same zeolite, i.e. by lengthening (or shortening) the diffusional paths inside the pores, or by using another zeolite with slightly narrower (wider) pores. By contrast, case (iii) is an intrinsic chemical effect, and the selectivity will be independent of the crystal size.

Shape-selective catalysis in zeolites is already exploited in a number of large-scale processes [7]. In most cases, the observed selectivity effects can be rationalized satisfactorily in terms of the traditional classification outlined above. To account for more recent research results, however, a number of novel concepts for shape-selective catalysis in zeolites were advanced. Among these are cage or window effects, a directed (e.g. tip-on) adsorption of molecules at the active sites, secondary shape selectivity, inverse shape selectivity and pore mouth catalysis. For an adequate discussion of these and other concepts, the reader can be referred to Refs. [36,37].

6. Concluding remarks

Zeolite materials science is an advanced field, and the same is true for the use of zeolites in catalysis. Only a few fundamental aspects could be addressed in the present review, but the references cited offer the opportunity to the reader to acquire adequate, modern and in-depth information on a topic which is equally fascinating from a fundamental viewpoint and for industrial research. Zeolite catalysis is a good example for the impact and beneficial effects of novel materials on the performance and efficiency of industrial processes and, ultimately, the welfare of mankind. At the same time, zeolite catalysis is a truly interdisciplinary field which needs the expertise and ingenuity of mineralogists, crystallographers, chemists, physicists and engineers.

Catalysis is one of the most important fields of application of zeolites, but by no means the sole one. Zeolites are, besides, used on a large scale as ion exchangers in laundry detergents and for the clean-up of radioactive waste and as adsorbents for the purification and separation of numerous substances.

Large efforts are being undertaken worldwide to open the door to novel applications for zeolites, e.g. in electrochemistry, photochemistry, membrane science and technology, to enumerate only a few. Looking for such novel applications is equally fascinating as zeolite catalysis, but no doubt beyond the scope of this contribution.

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References

[1] P.B. Venuto, E.T. Habib Jr., in: Fluid Catalytic Cracking With Zeolite Catalysts, Marcel Dekker, New York, Basel, 1979, 156 pp.

[2] R. von Ballmoos, D.H. Harris, J.S. Magee, in: G. Ertl, H. Knözinger, J. Weitkamp (Eds.), Handbook of Heterogeneous Catalysis, Vol. 4, Wiley–VCH, Weinheim, 1997, p. 1955.

[3] J.E. Naber, K.P. de Jong, W.H.J. Stork, H.P.C.E. Kuipers, M.F.M. Post, in: J. Weitkamp, H.G. Karge, H. Pfeifer, W. Hölderich (Eds.), Zeolites and Related Microporous Materials: State of the Art 1994, Studies in Surface Science and Catalysis, Vol. 84, Elsevier, Amsterdam, 1994, p. 2197, Part C.

[4] J. Scherzer, A.J. Gruia, in: Hydrocracking Science and Technology, Marcel Dekker, New York, Basel, Hong Kong, 1996, 305 pp.

[5] S.T. Sie, in: G. Ertl, H. Knözinger, J. Weitkamp (Eds.), Handbook of Heterogeneous Catalysis, Vol. 4, Wiley–VCH, Weinheim, 1997, p. 1998.

[6] F.G. Dwyer, in: W.R. Moser (Ed.), Catalysis of Organic Reactions, Marcel Dekker, New York, Basel, 1981, p. 39.

[7] N.Y. Chen, W.E. Garwood, F.G. Dwyer, in: Shape Selective Catalysis in Industrial Applications, Marcel Dekker, New York, Basel, 1989, p. 203.

[8] P.B. Venuto, Microporous Materials 2 (1994) 297.

[9] M.E. Davis, Microporous and Mesoporous Materials 21 (1998) 173.

[10] W. Löwenstein, Am. Mineralogist 39 (1954) 92.

[11] D.H. Everett, Pure Appl. Chem. 31 (1972) 585.

[12] J.C. Vartuli, W.J. Roth, J.S. Beck, S.B. McCullen, C.T. Kresge, in: H.G. Karge, J. Weitkamp (Eds.), Molecular Sieves — Science and Technology, Vol. 1, Springer Verlag, Berlin, Heidelberg, New York, 1998, p. 97.

[13] F. Liebau, in: Structural Chemistry of Silicates — Structure, Bonding and Classification, Springer Verlag, Berlin, Heidelberg, New York, Tokyo, 1985, 347 pp.

[14] F. Liebau, H. Gies, R.P. Gunawardane, B. Marler, Zeolites 6 (1986) 373.

[15] H. Gies, B. Marler, U. Werthmann, in: H.G. Karge, J. Weitkamp (Eds.), Molecular Sieves — Science and Technology, Vol. 1, Springer Verlag, Berlin, Heidelberg, New York, 1998, p. 35.

[16] A. Dyer, in: An Introduction to Zeolite Molecular Sieves, John Wiley and Sons, Chichester, 1988, p. 1.

[17] R. Szostak, in: H.G. Karge, J. Weitkamp (Eds.), Molecular Sieves — Science and Technology, Vol. 1, Springer Verlag, Berlin, Heidelberg, New York, 1998, p. 157.

[18] J.A. Martens, P.A. Jacobs, in: J. Weitkamp, L. Puppe (Eds.), Catalysis and Zeolites, Springer Verlag, Berlin, Heidelberg, New York, 1999, p. 53.

[19] W.M. Meier, D.H. Olson, Ch. Baerlocher, in: Atlas of Zeolite Structure Types, 4th Edition, Elsevier, London, 1996, 229 pp.

[20] E.F. Vansant, in: Pore Size Engineering in Zeolites, John Wiley–Salle-Sauerländer, Chichester–Aarau, 1990, p. 145.

[21] G. Kühl, in: J. Weitkamp, L. Puppe (Eds.), Catalysis and Zeolites, Springer Verlag, Berlin, Heidelberg, New York, 1999, p. 81.

[22] J. Weitkamp, P. Kleinschmit, A. Kiss, C.H. Berke, in: R. von Ballmoos, J.B. Higgins, M.M.J. Treacy (Eds.), Proceedings from the Ninth International Zeolite Conference, Vol. 2, Butterworth–Heinemann, Boston, 1993, p. 79.

[23] G. Perego, R. Millini, G. Bellussi, in: H.G. Karge, J. Weitkamp (Eds.), Molecular Sieves — Science and Technology, Vol. 1, Springer Verlag, Berlin, Heidelberg, New York, 1998, p. 187.

[24] G. Bellussi, C. Perego, in: G. Ertl, H. Knözinger, J. Weitkamp (Eds.), Handbook of Heterogeneous Catalysis, Vol. 5, Wiley–VCH, Weinheim, 1997, p. 2329.

[25] H.K. Shin, H. Hirabayashi, H. Yahiro, M. Watanabe, M. Iwamoto, Catal. Today 26 (1995) 13.

[26] A. Fritz, V. Pitchon, Appl. Catal. B: Environmental 13 (1997) 1.

[27] H.G. Karge, in: H. Chon, S.-K. Ihm, Y.S. Uh (Eds.), Progress in Zeolite and Microporous Materials, Studies in Surface Science and Catalysis, Vol. 105, Elsevier, Amsterdam, 1997, p. 1901, Part C.

[28] P.A. Jacobs, E.G. Derouane, J. Weitkamp, J. Chem. Soc. Chem. Comm. (1981) 591.

[29] E.N. Coker, J.C. Jansen, in: H.G. Karge, J. Weitkamp (Eds.), Molecular Sieves — Science and Technology, Vol. 1, Springer Verlag, Berlin, Heidelberg, New York, 1998, p. 121.

[30] G.H. Kühl, J. Phys. Chem. Solids 38 (1977) 1259.

[31] H.G. Karge, M. Hunger, H.K. Beyer, in: J. Weitkamp, L. Puppe (Eds.), Catalysis and Zeolites, Springer Verlag, Berlin, Heidelberg, New York, 1999, p. 198.

[32] R.M. Lago, W.O. Haag, R.J. Mikovsky, D.H. Olson, S.D. Hellring, K.D. Schmitt et al., in: Y. Murakami, A. Iijima, J.W. Ward (Eds.), New Developments in Zeolite Science and Technology, Studies in Surface Science and Technology, Vol. 28, Kodansha/Elsevier, Tokyo/Amsterdam, 1986, p. 677.

[33] J.A. Rabo, G.J. Gajda, in: D. Barthomeuf, E.G. Derouane, W. Hölderich (Eds.), Guidelines for Mastering the Properties of Molecular Sieves, NATO ASI Series B, Vol. 221, Plenum Press, New York, 1990, p. 273.

[34] V.L. Zholobenko, D.B. Lukyanov, J. Dwyer, W.J. Smith, J. Phys. Chem. B 102 (1998) 2715.

[35] J. Weitkamp, M. Breuninger, H.G. Karge, M. Hunger, in: M.M.J. Treacy, B.K. Marcus, M.E. Bisher, J.B. Higgins (Eds.), Proceedings of the 12th International Zeolite Conference, Materials Research Society, Warrendale, Pennsylvania, 1999, p. 2697, Part IV.

[36] J. Weitkamp, S. Ernst, L. Puppe, in: J. Weitkamp, L. Puppe (Eds.), Catalysis and Zeolites, Springer Verlag, Berlin, Heidelberg, New York, 1999, p. 327.

[37] P. Espeel, R. Parton, H. Toufar, J. Martens, W. Hölderich, P. Jacobs, in: J. Weitkamp, L. Puppe (Eds.), Catalysis and Zeolites, Springer Verlag, Berlin, Heidelberg, New York, 1999, p. 377.