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2-Dimensional Zeolites

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Introduction

Zeolites are crystalline silica-based microporous materials with pore sizes ranging from 0.25 to more than 1 nm. Until now, approximately 215 zeolite topologies have been reported (http://www.iza-online.org/)[1] while many others are possible[2,3] and for each topology, many varieties of framework composition are feasible. Although zeolite catalysts and adsorbents are used in numerous commercial applications, there are long-standing and emerging challenges in catalysis, adsorption and membrane separations as well as nontraditional applications in energy storage, electronic and optical materials (discussed at an earlier perspective in this journal)[4] that cannot be fully met by the currently available microporous materials. For example, it has long been recognized that precise placement of active sites within a hierarchy of pore networks is crucial to achieve control of molecular traffic and interconversion, as needed for optimal performance in separations and catalysis.[5] However, precisely assembled hierarchical catalysts remain elusive.[6,7] Similar unmet challenges exist in synthesizing selective adsorbents and membranes with molecularly-sized diffusion lengths to enable energy efficient ultrafast pressure and temperature swing-adsorption processes and high-flux molecular sieve membrane separations, respectively.[8–10] Many of these synthetic goals can be accomplished by using nm-thick zeolite layers (which can be called 2-dimensional zeolites) organized as (1) pillared assemblies, and (2) films.[11–16]

Over the last 20 years, research on synthesis and characterization of 2-D zeolite layers and on methods for their manipulation by exfoliation and pillaring resulted in important developments in the areas of catalysis and separations and to an emerging toolbox for nanotechnology applications of molecular sieves. This article provides a brief, and, therefore, incomplete, historical overview, followed by discussion of recent progress and emerging ideas for future research and development of 2-D zeolites and related materials. It is argued that it is now possible to establish a palette of 2-D nanoporous materials, precisely determine their crystal structure and understand their thermal and chemical stability, as well as mechanical, adsorption and transport properties and use this understanding to generate novel high-performance materials. Envisioned applications include purification and separation processes, adsorption and catalysis.

From layered precursors to pillared and exfoliated zeolites

In 1994, Mobil researchers reported the synthesis of the zeolite MCM-22 by thermally driven topotactic condensation of a layered precursor, called MCM-22(P), which consists of single-unit-cell thick ($\sim$2 nm) layers.[17] During thermal treatment, the terminal Si-OH groups of a layer condense with the corresponding groups of the neighboring layers to form Si-O-Si linkages (Figure 1, top right). The 3-D zeolite framework created was given the framework code MWW. The discovery of the MWW layered zeolite precursor stimulated further works on swelling, pillaring by various oxide pillars[18] including, more recently, single atom insertions (called interlayer expansion)[19] and, most importantly for this discussion, exfoliation (Figure 1). The first method of exfoliation to create a 2-D zeolite was reported in 1998 and consisted of swelling MCM-22(P) with a surfactant under strong basic conditions, followed by washing in acidic solution and sonication.[11] The resulting suspension contained 2-D crystalline fragments. It was demonstrated by TEM imaging that the 2-D MWW exfoliated layers have the expected 2 nm thickness and a structure as depicted in Figure 1 (bottom right). They contain a bi-dimensional pore system that runs within the plane of the layers with openings defined by 10 SiO_4-tetrahedra (called 10-member rings: 10MR). There are no connected pores running through the layers (due to 6MR transport limiting apertures), but the external surface contains 12MR pockets with unique properties, which can serve as adsorption and catalytic sites for bulky molecules.

Since the discovery of MWW and its layered precursor, several other layered (alumino) silicate zeolite precursors have been discovered and described in recent comprehensive reviews.[20,21] In parallel, nonaluminosilicate layered molecular sieves including many layered aluminophosphates[22] and metal-organic-frameworks (MOF)[23] have been reported,

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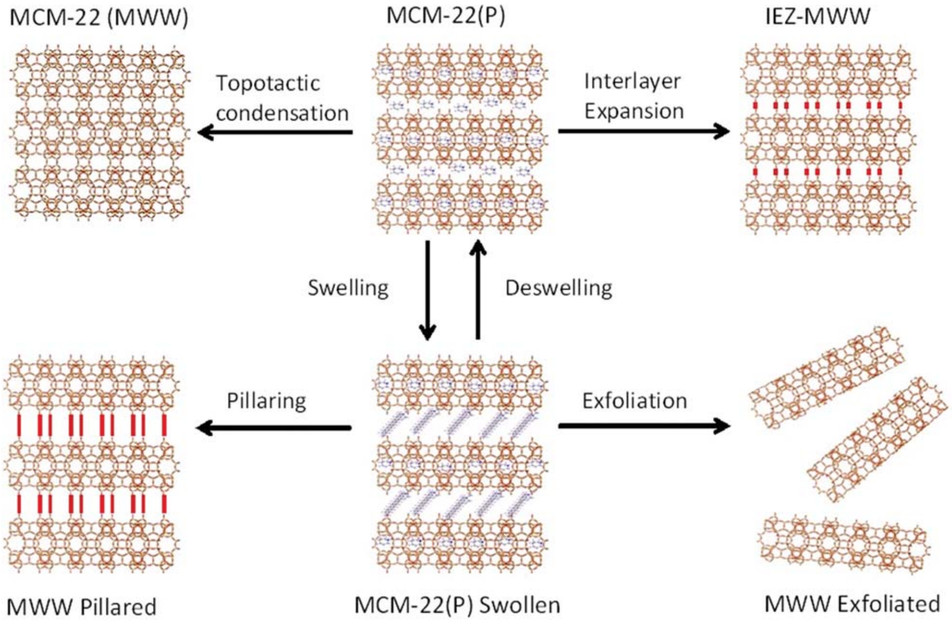

Figure 1. Schematic of MCM22-P and derivative materials (see text) including the first exfoliated zeolite.

further expanding the range of available materials that could possibly be exfoliated to generate 2-D zeolites or zeolite analogues.

Among the aluminosilicate frameworks that have been prepared as layered precursors, the layered MFI framework, called multilamellar MFI (Figure 2) is of exceptional importance because (1) the 3-D framework corresponds to the structure of the zeolite ZSM-5, one of the most widely used zeolites in industrial catalysis, and (2) the 2-D layers contain 10MR pores running within but also (and unlike MWW) through the layers. The latter is a very important characteristic of multilamellar MFI, because the 10MRs running

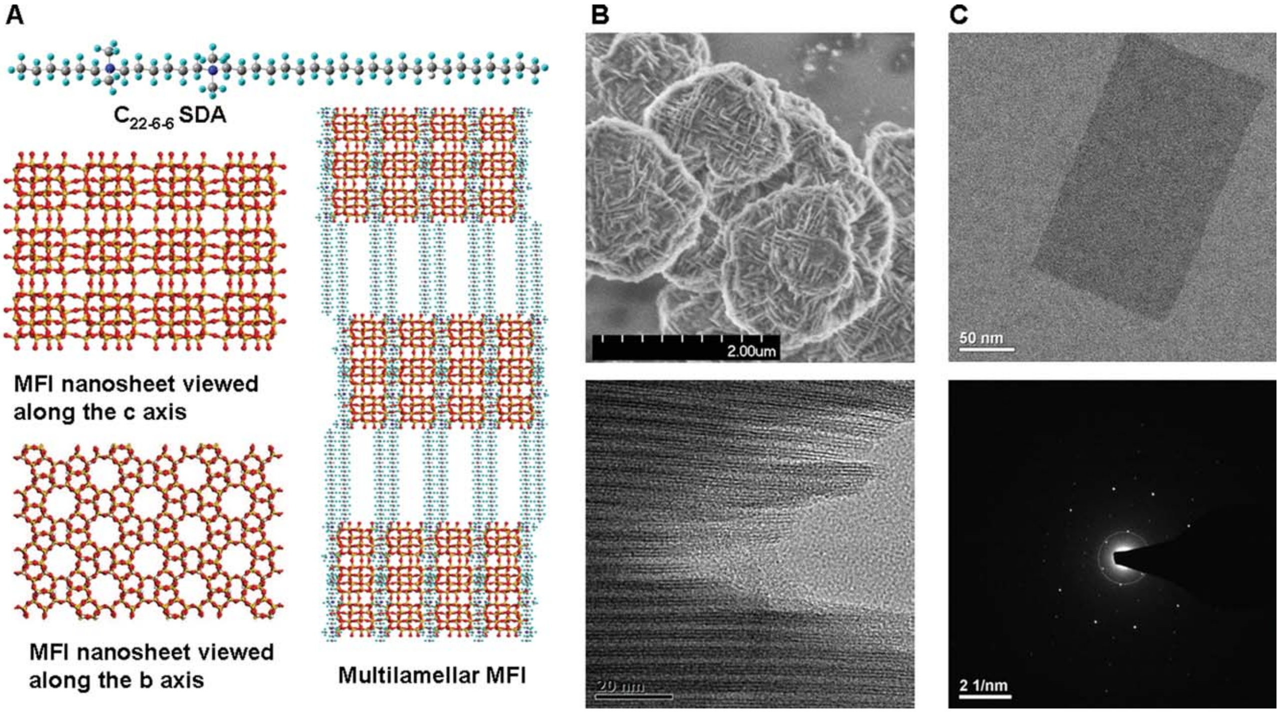

Figure 2. Multilamellar MFI structure (A) and corresponding SEM and TEM images (B), and part (C) shows a TEM image (top) and electron diffraction (ED, bottom) of a typical exfoliated 3 nm-thick MFI layer.

through the layers provide access to the shape-selective interior of the layers while reducing the characteristic length for diffusion to the 1 nm scale. It took 40 years from the discovery of the MFI framework[24] to realize its layered precursor (multilamellar MFI) consisting of 2–3 nm-thick layers.[12] This long-awaited breakthrough was achieved by Ryoo and coworkers using structure directing agents (see SDA, shown at the top of Figure 2A) capable of *dual templating*. It appears that the di-quaternary ammonium portion (the two N atoms are shown in Figure 2A in dark blue) of the surfactant templates the MFI layer pore structure, while the long tail serves as a space-filler between the MFI layers (see Figure 2A, right schematic). The thin dimension of the zeolite layers corresponds to the *b*-axis of MFI, which contains straight 10MR pores (see Figure 2A bottom left). Scanning (SEM) and transmission (TEM) electron microscopy (Figure 2B top and bottom, respectively) reveal micrometer-sized particles consisting of intergrown plates, which in turn consist of 3 nm-thick layers. Unlike MWW, multilamellar MFI is already swollen after synthesis since part of the SDA is anchored in the interior or associated with the zeolite layer surface and part of it extends outside the layers. Therefore, multilamellar MFI does not require swelling before pillaring[13] and exfoliation.[16]

Although the MWW and MFI layers are not single-atom thick, they represent (or approach) the smallest possible thickness required to define the crystal and pore structure of the corresponding frameworks. Their single (or near single)-unit-cell thickness formally qualifies them as 2-D materials from the crystallographic standpoint, i.e., based on the absence of periodicity of the structure in the third dimension (for a discussion of different definitions of dimensionality in nanomaterials see reference[25]) and opens new opportunities to control molecular transport with nm-accuracy by their precise manipulation and assembly. Moreover, the fact that these two frameworks are stable at such small dimensions points to the possibility of preparing even thinner porous networks based on zeolites and zeolite analogues like aluminophosphates and metal-organic frameworks, with the ultimate limit and outstanding synthetic challenge being a 2-D single-atom thick porous net.

2-D zeolites for thin films

In 2003, we introduced the idea of using exfoliated zeolite layers for thin film and nanocomposite applications.[26] *For such applications, a high-aspect ratio, preservation of crystal (and pore) structure, thickness and aspect ratio uniformity, and elimination of amorphous and nonexfoliated contaminants are of paramount importance.* It took five years to realize that these properties could not be fulfilled by the previously reported, solution-based, exfoliation methods and to develop a new exfoliation methodology based on melt blending with a polymer, which ensured structure preservation of the exfoliated layers.[27]

Removal of the polymer and purification of the 2-D zeolites from nonexfoliated particles turned out to be a challenging problem, which was solved by the development of gradient centrifugation methods combined with selection of appropriate solvents.[15] Our approach to prepare 2-D zeolite suspensions of MWW and MFI is summarized schematically in Figure 3. Currently, it is the only method that can provide high purity 2-D zeolite nanosheet suspensions. A typical TEM image and the corresponding electron diffraction pattern are shown in Figure 2C, confirming that the layers are indeed crystalline and have the expected crystal and pore structure. The cover illustration shows a low-magnification TEM image of 2-D MFI nanosheets along with a high-resolution inset with a superimposed structural model. Some nonexfoliated particles and twinned nanosheets are also evident in this image and for certain applications may be detrimental. As we recently reported in this journal,[15] for membrane formation applications removal of these nonexfoliated particles is necessary and it can be accomplished by centrifugation, albeit with considerable yield loss.

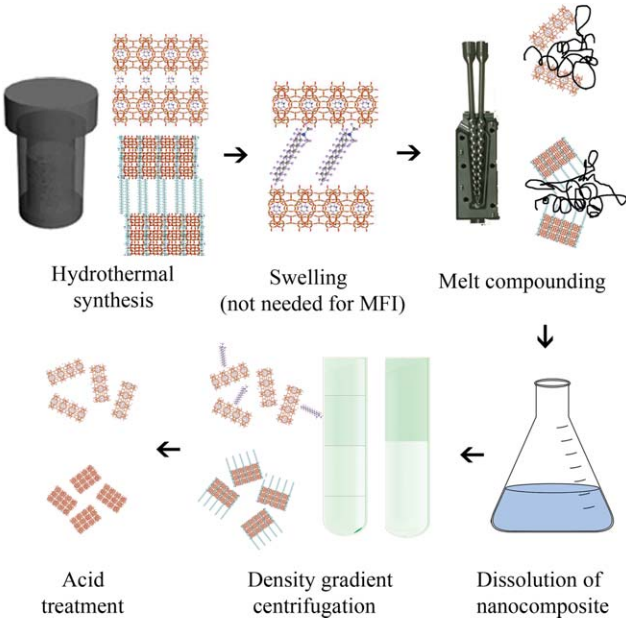

Figure 3. Schematic of method to form 2-D zeolites MWW and MFI.

After forming suspensions of these highly purified 2-D zeolite nanosheets in organic solvents, we can use filtration of the suspensions through porous supports (e.g., porous alumina, silica, etc.) to deposit compact multilayers of nanosheets as thin as 100 nm (ca. 30 nanosheets stacked on top of each other). The nanosheets, remain at the support surface and form oriented coatings since they deposit with their short dimension perpendicular to the support surface. However, the deposits contain nm-sized pinhole defects, which should be eliminated for uses such as separation membranes. This is accomplished by mild secondary solvothermal growth aiming to close such defects while keeping thickness at a minimum. Preferred orientation is established by the orientation of deposited nanosheets, and its preservation during secondary growth is ensured using appropriate structure directing agents and other principles outlined in our earlier work.[10] The current state-of-the-art (Figure 4) is films $\sim$100 nm thick (10 times thinner than typical zeolite membranes), which exhibit record high fluxes and high selectivities for industrially important separations (e.g., of xylene isomer

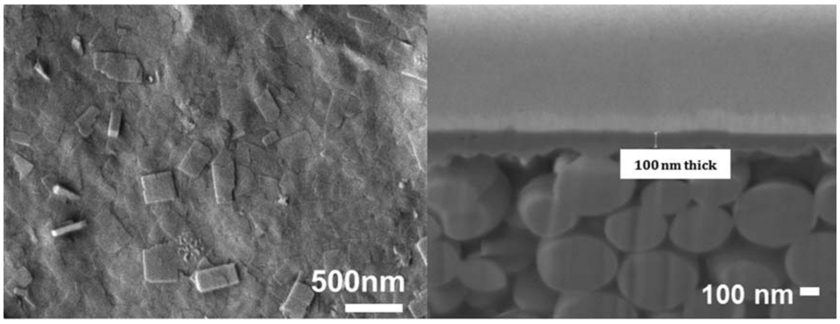

Figure 4. Scanning electron microscopy top (left) and cross section (right) images of 100 nm-thick membrane, made by secondary growth of deposited nanosheets.

mixtures). However, there is considerable room for improving membrane throughput by reducing membrane thickness, proportionally. Since the layer thickness is 2–3 nm, films as thin as 10 nm should be feasible, provided that compact-enough layers can be deposited. In order for this to be achieved, efforts to increase nanosheet aspect ratio (by optimizing solvothermal synthesis), and improve their aspect ratio uniformity (by novel separation and purification methods) are underway.

The filtration approach works very well for deposition on porous supports and has the advantage of wasting hardly any of the valuable (see the laborious and time-consuming process of Figure 3) exfoliated 2-D zeolite nanosheets and of ensuring uniform preferred orientation of nanosheets. However, it is not applicable for nonporous supports. Nanosheets on nonporous supports are of interest for low-dielectric constant materials,[28] for selective sensing,[29] and for fundamental studies of nanosheet structure, electronic, mechanical,[30] adsorption and transport properties.[31–33]

Future efforts should be directed toward developing deposition techniques for quantitative transfer of zeolite nanosheets to nonporous supports. Such deposition methods (e.g., Langmuir-trough deposition), coupled with improvements on aspect ratio mentioned earlier, may also allow manipulation and deposition of single 2-D zeolite nanosheets on nanofabricated supports, as it was recently achieved for graphene.[34] For example, Figure 5 shows a concept that if realized, it will allow, for the first time, transport measurements through nanometer-thick precisely sized micropores. These measurements will be extremely valuable since, by probing directly pore mouth adsorption and desorption, they will provide reliable estimates for mass transport resistances for zeolite membranes at the ultimate limit of single-unit-cell thickness. They can be combined with structural characterization by atomic force microscopy and X-ray diffraction (to quantitate local and global nanosheet distortions due to support, thermal and adsorption-induced stresses) and evaluation of mechanical properties (currently, only available for large zeolite crystals) to provide a complete picture of 2-D zeolite structure–property relations. Moreover, mixed multilayers with other types of nanosheets (e.g., graphene, metal-organic frameworks) are now possible. For example, surface functionalization using the terminal Si-OH groups of the nanosheets could be implemented to achieve controlled multilayer growth when two types of nanosheets with oppositely charged or otherwise appropriately functionalized surfaces are combined in sequential depositions. With appropriate selection of functional groups, it may be possible to create multilayers consisting of nanosheets in crystallographic registry. Such multilayers could be amenable to topotactic condensation during thermal treatment creating novel multifunctional materials.

Finally, from the practical engineering standpoint, it is now possible to revisit the concept of matrix/microporous-layer nanocomposites.[35] According to this concept, the 2-D microporous layers can be incorporated in polymer or inorganic porous matrices to achieve mixed-matrix microstructures, which, by combining the processability of polymers with the molecular sieving properties of the 2-D zeolite porous layers, may find applications as separation membranes. Prior attempts to realize this concept were not successful because they either relied on thick zeolite flakes, or nonexfoliated zeolites or exfoliated 2-D zeolites of which the structure was altered during exfoliation.

Hierarchically assembled 2-d zeolites for catalysis and adsorption

After isomorphic substitution of Si with other elements, for example Al, B, Ga, Ge, Fe, P, Sn and Ti, or by replacement of oxygen framework atoms with carbon, nitrogen or other functional groups, zeolites can provide confined adsorption and catalytic sites, including ones for oxidation as well as Brönsted and Lewis acid catalysis.[36–46] It is the interaction of guest molecules with these sites under micropore confinement that gives to zeolites their unique capabilities as selective catalysts and adsorbents. However, it is well established that in order to optimize adsorption and reaction selectivity and

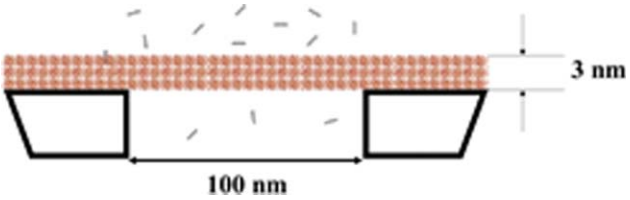

Figure 5. Schematic of nanofabricated zeolite nanosheet membrane concept with 3 nm-thick 2-D zeolite MFI and molecules of *n*-nonane permeating through the membrane.

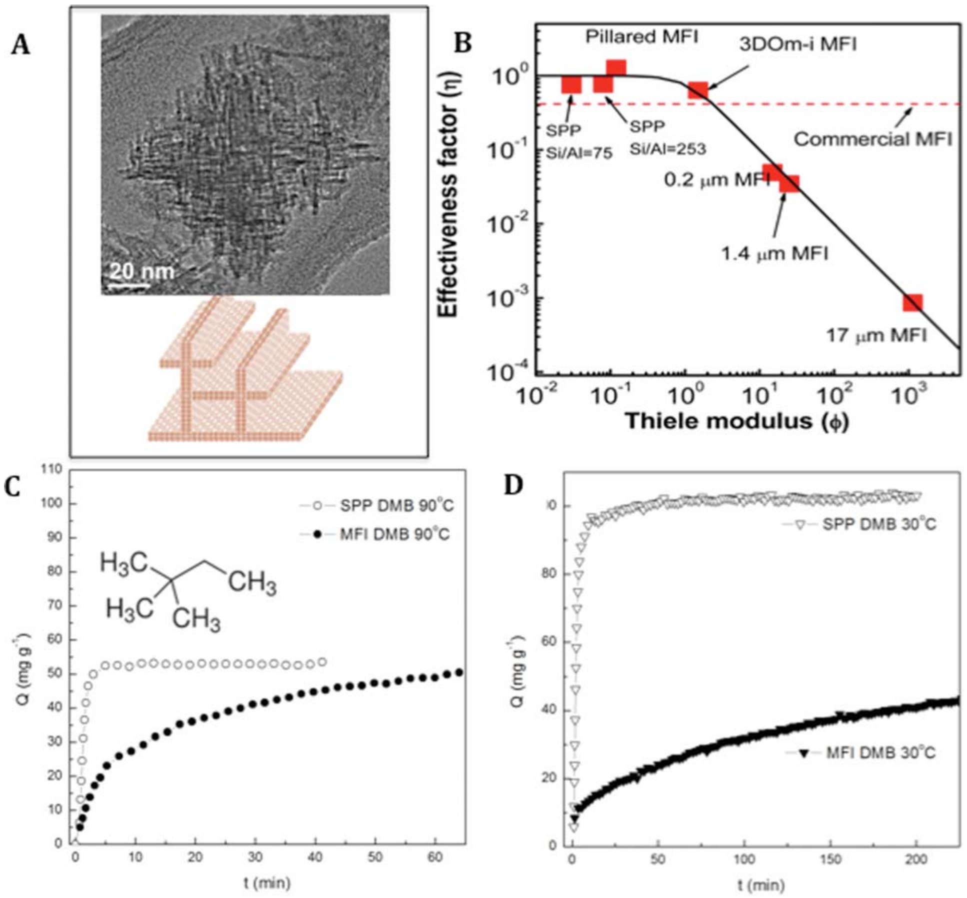

Figure 6. (A) Transmission electron microscopy (TEM) image of self-pillared pentasil (SPP) zeolite and schematic of its structure: MFI 2-D layers connected at branching points with MEL, (B) effectiveness factor vs. Thiele modulus plot for etherification of benzyl-alcohol for zeolite domain characteristic dimensions ranging from micrometers to nanometers (from Ref. 14), (C) and (D) 2,2-dimethylbutane adsorption at 90 and 30°C on SPP and conventional MFI nanocrystals. Adsorption is much faster in SPP. Equilibrium adsorbed amount is larger for SPP at 30°C and larger for conventional MFI at 90°C (see Refs. 47 and 48).

productivity, active site design is not sufficient. Manipulation of the hierarchy of length scales from the sub-nm to the mm level is required. Although there are numerous approaches to create hierarchical materials, the long-standing synthetic challenge to control their structure at the unit- or subunit-cell dimension (typically for most zeolites, 0.5-5 nm), can potentially be accomplished by few.

Pillaring of layered zeolite precursors is one of the few approaches capable to create hierarchical catalysts and adsorbents with single-unit-cell zeolite domains. Pillared zeolites, combine fast transport through mesopores and access to zeolitic pockets (as is the case for MWW) or to zeolite micropores with very short (nm scale) diffusion length (as is the case with pillared multilamellar MFI). However, pillaring relies on the availability of a layered precursor, introduces extra processing steps, and dilutes the zeolite by the introduction of the nonzeolitic pillar. To avoid these limitations, we introduced a novel, one-step synthesis approach to create single-unit-cell hierarchical zeolites, which we call self-pillared zeolites, by connecting 2-D zeolite nanosheets in a house-of-cards arrangement.[14] The connections are based on rotational intergrowths or other branching crystal growth mechanisms. This approach has been demonstrated for MFI and the resulting material was named SPP (self-pillared pentasil) to reflect the argument that the orthogonal connections between MFI nanosheets are made by coherently connected single-unit-cell needles of the related, but higher symmetry, pentasil zeolite MEL (Figure 6A). At a conceptual level this approach treats zeolite structures as building blocks that can be connected to each other, with a certain zeolite unit playing the role of connector at the branching points. Since faulting in zeolite structures is very common, in ongoing work, we attempt to extend this approach to other zeolites by identifying and exploiting their corresponding branching mechanisms.

Depending on the reaction, 2-D zeolites can potentially exhibit drastically different catalytic performance compared to conventional zeolites due to pore diffusion and pore entry effects and due to external, pore mouth and internal catalytic activity differences. These effects are not yet fully understood and require careful characterization and assessment of catalytic sites coupled with quantitative description of adsorption and transport phenomena. For example, it has been clearly demonstrated (e.g., by deactivation the external surface and mathematically analyzing reaction-diffusion coupling— see Figure 6B) that despite many orders of magnitude differences in observed rates due to diffusion limitations, intrinsic Brönsted acid catalytic activity in the micropores of 2-D zeolites is indistinguishable from that in conventional catalysts.[14] However, it is unclear if this finding could be generalized for other types of catalytic and adsorption sites. Also, for larger molecules that either cannot or can only partially fit in the micropores, differences are to be expected.

Only by systematic variation of internal microporosity and external surface structure of 2-D zeolites, these new adsorption and catalytic phenomena can be identified and quantitatively understood. As an example, Figures 6C and D show results from a study of 2,2-dimethylbutane (2,2-DMB) adsorption in MFI nanosheets (2 nm thick) vs. conventional (crystal size 30–50 nm) MFI at two temperatures (30 and 90°C). 2,2-DMB is relatively bulky and fits tightly in the channels of the zeolite MFI. It diffuses slowly and adsorbs preferentially at the MFI channel intersections. Reassuringly, the short diffusion length of nanosheets enhances its rate of adsorption at both temperatures in quantitative agreement with expectations from diffusion theory. However, interesting differences are observed in equilibrium adsorption behavior. Specifically, at the higher temperature, adsorption at equilibrium is higher for the conventional zeolite, while at the lower temperature, enhanced adsorption at equilibrium is exhibited by the self-pillared 2-D zeolite. Other molecules with sizes comparable to the thickness of the nanosheets (e.g., *n*-nonane) show a decrease of the amount adsorbed at equilibrium at certain low pressures, while at higher pressures their adsorption exceeds that of conventional MFI,[47] i.e., they exhibit a crossover behavior. Recently, a molecular simulation study showed that this unusual crossover behavior could be attributed to a general multi-step mechanism.[48] These and other recent results indicate that systematic adsorption and reaction measurements using a variety of hydrocarbons (representative of molecules encountered in petrochemical processing) and oxygenates (representative of molecules encountered in biomass processing) over a wide range of temperatures and pressures on pillared 2-D zeolites are warranted. They should be combined with molecular simulations to elucidate how new adsorption and eventually reaction properties may emerge. It is in this context that single-unit-cell zeolite nanosheets may enable a paradigm shift methodology to control not only zeolitic structure but also adsorption and catalytic function at the nanoscale.

Of fundamental and practical significance for catalysis and adsorption applications is the question of thermal, hydrothermal and chemical stability of zeolite nanosheets. Their high-surface area and short diffusion distances may make these materials more vulnerable than conventional zeolites and limit their potential uses.[49] Therefore, systematic studies to determine their stability, along with development of functionalization or encapsulation methods to improve it in environments known to be corrosive for zeolites (e.g., contact with water or steam) should be pursued.

Outlook

Conceptually, running a sharp knife through the crystal structure model of any zeolite structure-type can create 2-D zeolites. From the myriad possibilities, at least two (MWW and MFI) have been demonstrated to exist as stable self-standing nanosheets, with well-defined microporous structures within and through the layer. It should now be possible to extend the list of 2-D zeolites and related materials and explore uses as building blocks of hierarchical materials, nanocomposites, and thin films.

Depending on the structure, 2-D zeolites allow uniform and precise control of diffusion length down to the nm scale. They also exhibit crystallographically defined surface landscapes featuring nm-sized periodicity and intriguing coupling of “external” and “internal” surfaces at the pore mouths. These properties are not available in other 2-D materials and in conventional zeolites and may allow catalysis for bulky molecule transformations (for example, reactions of carbohydrates) by reducing deactivation and enabling cascade reactions.[50]

Current challenges that limit wide implementation of these materials are the lengthy, costly and low-yield synthesis and purification procedures, the relatively small and nonuniform aspect ratio of the nanosheets, and the loss of order and porosity during exfoliation for certain structures, especially those approaching “single-atom” thickness. Moreover, assembly and coating techniques to deposit these single-unit-cell nanosheets and make functional devices are lagging behind compared to other 2-D materials, while predictive, simulation-based, structure–property relations accounting for the synergism of internal and external surfaces are not yet available.

After two decades of steady progress, 2-D zeolites seem to be in an era ripe for fundamental studies and technological breakthroughs. Their near term impact will most likely be as seeds for growth of oriented zeolite films or as components of composites for the fabrication of novel high-throughput, energy efficient membranes for processes such as separations in the petrochemical- and biorefinery (e.g., xylene and butane isomer separations, and ethanol or butanol dehydration, respectively).

Acknowledgments

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