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Diversity of Layered Zeolites: From Synthesis to Structural Modifications

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Abstract:

In recent years, great efforts have been devoted to synthesize and modify layered zeolites, a new family of microporous crystalline materials that are viewed as covalently bonded continuous frameworks extended in only two dimension. This leads to a very interesting and attractive research area in porous material science, since the stacking modes of zeolite layers could be constructed into various types of structure by direct synthesis or postsynthetic treatments, endowing zeolitic materials with structural diversity. The potential of layered zeolite precursors for generating hierarchical catalysts or incorporating organic functional groups into two dimensional structure is of particular interests. In this contribution, the most attractive achievements in the research area of layered zeolites are summarized, including synthetic approaches, strategies for modifications of layered structures and catalytic applications. Last but not least, the challenges for future researches on this type of porous materials are proposed.

1. Introduction:

Zeolites are crystalline microporous materials formed by SiO₄ and AlO₄ corner-sharing tetrahedral as primary building units, forming three-dimensional (3D) frameworks with well-defined channels and cavities of molecular dimensions. The void space within the crystalline allows zeolites to discriminate molecules based on their sizes or

geometric shapes.¹⁻² With variable chemical compositions and unique pore topologies, zeolites have been utilized in a wide range of industrial applications, such as catalysts in the processes of oil refining and fine chemicals synthesis.³⁻⁵ Zeolites are typically synthesized *via* hydrothermal/solvothermal/ionothermal approaches, and also sometimes the syntheses are performed through the dry-gel,⁶ microwave-assisted,⁷ or solvent-free route.⁸ It is possible to yield zeolite materials with 3D architecture by thermal synthesis reactions, but sometimes two-dimensional (2D) zeolites with layered structures are obtained.⁹⁻¹⁴ Alternatively, recent research reveals that it is possible to postsynthesize 2D zeolitic materials from the 3D zeolite structures already constructed in hydrothermal synthesis *via* removing or rearranging selectively certain specific building blocks.¹⁵

The layered zeolites have been viewed as covalently bonded continuous frameworks extended in two dimension, whereas the crystal growth is constrained in the third direction simultaneously. The zeolite layers interconnected with each other through the hydrogen bonding between silanol groups on the layer surface and the possible ionic/hydrogen bonding with the organic template molecules occluded between the layers. The 2D layered zeolite precursors could be transformed into the fully tetrahedral connected 3D framework through interlayer condensation after removing the organic species by calcination (Figure 1).

Up to now, there are 231 unique framework structures identified by the International Zeolite Association.¹⁶ Among them, 14 types of zeolite structures have been recognized to have corresponding layered precursors so far. Moreover, a specific zeolite structure may correspond to a variety of layered precursors as a result of different framework compositions or synthesis conditions. For instance, the representative layered precursor of MWW structure could be MCM-22P,¹⁷ SSZ-25,¹⁸ PHS-3,¹⁹ ERB-1P,²⁰ ITQ-1P,²¹ Ti-MWW-P,²²⁻²³ *etc.* The typical layered zeolitic precursors and their corresponding 3D structure are listed in Table 1.¹⁷⁻⁴²

The most attractive characteristic of layered zeolites is that the stacking mode of their constructing layers is highly plastic, and they are amenable to postsynthetic modifications by various techniques. Then various zeolitic materials can be derived to possess more open structures, such as porous materials with swollen,⁴³ pillared,⁴⁴ fully or partially delaminated⁴⁵⁻⁴⁶ and interlayer-expanded structures.⁴⁷ Compared to the

conventional parent layered zeolites, the stacking mode of layers in postsynthesized materials has experienced great changes. These novel materials retained the crystalline structure of traditional layered zeolite, but the accessibility of the layers has been greatly enhanced, which makes them become a special type of hierarchical materials. As hierarchical catalysts have shown remarkable catalytic behaviors in many promising processes,⁴⁸⁻⁵⁰ the rational synthesis of zeolite catalysts with hierarchical architecture from layered zeolite perspective has attracted great academic and industrial interests. On the other hand, the hierarchical structure in the resulting layered zeolites provides the possibility of introducing additional bulky functional groups into zeolite catalysts.

Nowadays, layered zeolites are becoming attractive intermediate materials for designing versatile functional materials and hierarchical catalysts. In this contribution, we will present the research progress in the field of layered zeolites, including the achievements in the preparation, post-synthesis modifications of layered precursor as well as their catalytic applications.

2. The synthesis

Generally, layered zeolites with 2D structure are a special kind of materials in zeolite family. After removing the organic templating species occluded in the interlayer voids by calcination, the neighboring layers are condensed to form the corresponding 3D zeolites with complete/incomplete structures. Most of the layered zeolites are obtained usually in the conventional hydrothermal synthesis. Additionally, recent studies have found that layered zeolites could also be prepared through hydrothermal synthesis by using specially designed bifunctional surfactants as organic structure-directing agent (OSDA)³⁹ or removal of specific building units in 3D zeolite through the “top-down” hydrolysis process.¹⁵ Thus, the synthesis of layered zeolite could be categorized into three different approaches: conventional hydrothermal synthesis, synthesis using bifunctional surfactants as OSDAs and post-rearrangement of the 3D zeolite framework.

2.1 Conventional synthesis

The first exciting breakthrough in the field of layered zeolite is the discovery of MWW-type layered zeolite precursor MCM-22P.¹⁷ The 2D MCM-22P is composed of the MWW layers with a uniform thickness of 2.5 nm and an ordered stacking sequence along *c* direction, meanwhile with the OSDA molecules possibly occluded between neighboring layers.

The calcination of precursor induces the interlayer condensation between layers, resulting in the regular MCM-22 with 3D framework. Besides 2D sinusoidal channels of 10-membered ring (MR) running throughout the structure parallel to the *ab*-plane, the 3D MWW structure also contains an independent channel system which is comprised of large supercages (0.7*0.7*1.8 nm) (Figure 2). The supercages turn to be pockets or cup moieties (0.7*0.7 nm) at the crystal exterior. Besides, the 3D zeolite with MWW structure (MCM-49) could also be directly synthesized without the formation of layered precursor by hydrothermal synthesis.⁵¹ Therefore, the synthesis of MCM-22 that could proceed along two different routes indicates that the 2D zeolite precursors are formed as intermediate before the condensation of individual layers to 3D zeolite.

The MWW structure was also found in many other precursors, such as PSH-3 (Puppe, 1984),¹⁹ SSZ-25 (Zones, 1987),¹⁸ ERB-1 (Bellussi, 1988),²⁰ ITQ-1 (Corma, 1995),²¹ Ti-MWW (Wu, 2001).²²⁻²³ It is worth mentioning that MWW structure was usually constructed in the presence of trivalent cations (aluminium or boron), that is, the direct preparation of the pure-silica and titanosilicate analogous was difficult to realize. The layered precursor of pure-silica MWW structure ITQ-1 was successfully synthesized with the aid of two organic templates such as trimethyladamantamonium hydroxide (TMAda⁺OH) and hexamethylenimine (HMI).²¹ Besides, the titanosilicate with MWW topology has been hydrothermally synthesized with the coexistence of boron and titanium using piperidine (PI) or HMI as OSDA. The Ti-MWW precursor can be obtained to have a Si/Ti ratio as low as 10 when the Si/B ratio of the gel is maintained as low as 0.75.²²⁻²³ Later, B-free Ti-MWW with 2D layered structure was successfully prepared through an innovative strategy of reversible structural rearrangement (Figure 3). First, the already synthesized ERB-1 was subjected to deboronation to give rise to a highly siliceous MWW zeolite (Si/B > 500). Then, the 3D silicate was treated with tetrabutyl orthotitanate (TBOT), which was hydrolyzed in an aqueous solution of amines, *e.g.* HMI, PI, pyridine, piperazine *etc.* After further hydrothermal treatment at elevated temperature, the B-free titanosilicate with 2D layered structure was obtained.⁵²

Besides, other layered materials containing MWW layers stacking in misalignment style were also reported, such as MCM-56,⁵³⁻⁵⁴ EMM-10P²⁵, SSZ-70.^{24,55} The possible arrangement of MWW layers and interaction between surface silanols has been theoretically investigated. The results

indicated that the MCM-56 may be constructed by relatively disordered MWW layers that are partially condensed.⁵⁶ Although the stacking models of these materials have been proposed, the real interaction mode of the surface silanols on the adjacent MWW layer is not yet well verified. Recent studies discovered an intergrown zeolite ECNU-5 composed of two different MWW polymorphs (ECNU-5A and ECNU-5B), which was synthesized from a rapid dissolution-recrystallization (RDR) route.⁵⁷ Structure elucidation verified that both polymorphs are built from the same MWW layers but different in the relative shift between adjacent layers (Figure 4). The unique geometry mismatch between the OSDA and 12-MR side pockets on the external layer surface is ascribed to causing the zeolite layer shift with half of the interlayer Si-OH groups to exist freely.

The early studies on MWW zeolites launched the discovery of the extensive family of distinct layered zeolites with other topologies. Except for MWW, most of the layered zeolites known were also obtained from conventional hydrothermal synthesis, such as layered precursors with FER,²⁶ CDO,²⁹ NSI,³² CAS topologies.³¹ Another typical example of layered zeolite is the materials with FER or CDO structure. They exist in the form of natural mineral, initially only in the form of 3D structure, but later their corresponding layered precursors were chemically synthesized. PREFER, a layered precursor containing ferrierite layers, was prepared by adopting a bulky template of 4-amino-2,2,6,6-tetramethylpiperidine in the fluoride media.²⁶ On the other hand, the CDO structure contains the same ferrierite layers as normal FER zeolite, but differences in the symmetry of layer connections, resulting in different pore structures. The FER zeolite has two intercrossed channels, 10-MR channel along *c* axis and 8-MR channel along *b* axis, while the CDO zeolite has an 8*8 MR intersection channel along *a* and *c* axis. FER and CDO structures can be regarded as the relative dislocation of the ferrierite layers (Figure 5). The former is constructed when the ferrierite layers are propagated by a mirror plane with *Immm* symmetry, but the latter, by translation with *Cmcm* symmetry.⁵⁸ The ferrierite layer is also found in other zeolite materials. MCM-47, synthesized with *bis*(*N*-methylpyrrolidinium)-1,4-butane as OSDA, contains the ferrierite layers and interlayer occluded organic species, but its structure cannot be readily calcined to form a condensed crystalline structure.²⁸ The ferrierite layer in PLS-3 and PLS-4 zeolites are stacked in the FER and CDO topology, respectively.²⁷ Moreover, the ferrierite layers also exist in ZSM-52,⁵⁹ ZSM-55,⁶⁰ ERS-12⁶¹, RUB-20, RUB-40⁶² and MCM-65⁶³ zeolites with different

layer substructures. Therefore, given a suitable OSDA, a crystalline material is formed that links all silanol groups. Otherwise, a disordered material is produced upon calcination. The similar phenomenon of layered zeolite containing the identical layer is also found in intergrown zeolites of NSI/CAS and RRO/HEU.

2.2 Surfactant-directed synthesis of layered zeolite

Most of the layered zeolites are obtained in the hydrothermal synthesis by chance, with the formation mechanism unclear. However, the layered precursor with MFI structure was successfully prepared with the aid of specially designed surfactants. Initially, the MFI structure is present in the form of 3D crystalline structure, and there is no corresponding 2D layered precursor reported. In 2009, Ryoo *et al.* first succeeded in the synthesis of layered MFI using various Gemini-type bifunctional surfactants as OSDAs (Figure 6), which were represented by $C_{22}H_{45}-N^+(CH_3)_2-C_6H_{12}-N^+(CH_3)_2-C_6H_{13}$.^{39,64-67} The surfactant exhibited dual structure-directing functionalities in two different length scale. The hydrophilic quaternary ammonium head directed the nucleation and growth of MFI structure, while the hydrophobic alkyl chain constrained the crystal growth beyond the ammonium region, resulting in the layered MFI zeolite with a single-unit-cell thickness. Additionally, further analysis indicated that the nanosheets were produced through a successive transformation from a hexagonal mesophase at the beginning to a multilamellar amorphous mesophase and finally to a lamellar zeolite framework. Interestingly, the thickness of MFI layers could be controlled by the number of the head ammonium groups.

This study opened up the possibility of hydrothermal synthesis of 2D layered zeolites with carefully designed bifunctional surfactants as OSDA. In principle the strategy appears to be applicable to all zeolite structures. Recently, the delaminated MWW layers was also successfully prepared by using the similar strategy as that reported by Ryoo.^{68,69} MIT-1 comprised of individual MWW layers was hydrothermally synthesized using a rationally designed OSDA, which had a hydrophilic head and hydrophobic tail.⁶⁸ Additionally, direct synthesis of MWW monolayers has been accomplished with the aid of dual templates, that is the long-chain surfactant and HMI. The head of surfactant was expected to be located in the cavities of the MWW layers, while the alkyl chain would avoid the linkages between layers. These types of organic surfactants were readily removed by calcination, leaving much of the interlayer space due to disordered assembly of MWW layers.⁶⁹

Thus, the calcined products (in the case of both MFI and MWW) often exhibit high surface area and large pore volume as compared to conventional 3D zeolites. This type of hierarchical structure built from disorderly packed zeolite layers has two advantages in catalytic applications: short diffusion pathway to the active sites for reactant molecules and more active sites exposed at the external surface. The FT-IR investigations have been carried out to study the distribution, acid strength, and steam stability of internal and external acid sites in layered MFI zeolite. The external active sites were weaker than the internal sites in acid strength, but exhibited remarkably higher steam stability than the internal acid sites (Figure 7).⁷⁰ Thus, the hierarchical zeolites composed of disorderly stacked nanolayers show promising catalytic behaviors in many reactions involving bulky reactants. The layered MFI nanosheets exhibited much longer lifetime in the methanol-to-hydrocarbon conversion than the conventional 3D ZSM-5 catalyst owing to the facile diffusion of coke precursors from the acid sites within the channels.³⁹ The silanols at the external surface of the layered MFI nanosheets could be used for the gas-phase Beckmann rearrangement of cyclohexanone oxime to ϵ -caprolactam, an important intermediate for the synthesis of Nylon-6.⁷¹ Moreover, titanosilicate MFI nanosheets (LTS-1) were tested in the selective oxidation of alkenes to epoxides with *tert*-butyl hydroperoxide, cumene hydroperoxide or aqueous H₂O₂. LTS-1 was more active than conventional titanosilicates for the reactions of bulky alkenes and oxidants and it was immune to Ti leaching and irreversible deactivation.⁷² This hierarchical MFI nanosheets were also suitable for Friedel-Crafts alkylation and acylation reactions containing small and bulky molecules.^{39,73-74}

On the other hand, recent studies have also reported the synthesis of the self-pillared MFI nanolayers with a "house of cards" morphology by adopting simple OSDA or various complex surfactants as templates.⁷⁵⁻⁷⁸ Tsapatsis and Okubo independently reported the synthesis of hierarchical MFI nanosheets, in which the zeolite layers are intergrown with the lamellar arranged perpendicular to each other (Figure 8).^{75,76} The unique arrangement of layered MFI zeolite nanosheets results in a hierarchical network of 2 - 7 nm mesopores. Besides, Che *et al.* have designed various amphiphilic molecules containing aromatic groups to directly synthesize single-crystalline mesostructured zeolite nanosheets. The geometrical matching between the arrangement of aromatic groups and the zeolitic framework induced the formation of MFI layers joined with a 90°

rotational boundary (Figure 9).⁷⁷⁻⁷⁸

2.3 Layer precursors obtained by 3D to 2D transformation

The above-mentioned 2D layered zeolites could transform into their corresponding 3D structure through the "bottom-up" (2D-to-3D) route. However, the inverse structural transformation, that is 3D-to-2D, is not common. An unusual case is that the reversible "top-down" transformation is observed on MWW-type titanosilicate with the assistance of proper amines.^{52,79-80} Recently, the synthesis of a novel organic-inorganic layered titanosilicate consisting of Ti-containing MWW-type nanosheets and PI ligands was reported through the "top-down" structural rearrangement.⁸⁰ Characterization results verified that the hydrothermal treatment with PI aqueous solution converted 3D Ti-MWW into the corresponding lamellar precursor, which contains unusual six-coordinated Ti active sites, without the framework dissolution and recrystallization process. The newly-generated Ti species, bearing an amine molecule as a ligand, exhibited an unprecedented high catalytic activity and recyclability in alkene epoxidation. This species could be responsible for the great enhancement in catalytic behavior, and the presence of a PI ligand suppressed the acidity of the hydroxyl groups, which then enhanced the product selectivity.

Except for that, there is almost no example reported in the family of conventional zeolites. However, if the 3D zeolite is constructed with the germanium (Ge) atom as basic building unit, the synthesis of layered zeolite may proceed through a "top-down" way.^{15,81}

The introduction of Ge into the zeolite synthesis allows the formation of numerous germanosilicates in various structures in the past years.⁸²⁻⁸⁶ The introduction of Ge could facilitate the formation of double four-ring (D4R) cages, because Ge-O-Ge or Si-O-Ge bond angles would be more suitable than Si-O-Si for stabilizing D4R unit. The presence of Ge in the framework endows germanosilicates with two distinct characteristics. Firstly, the distribution of Ge atoms is not uniform: Ge-rich D4R is often located in the connection between the two basic structural units. On the other hand, with respect to the Si-O bond, Ge-O bond is much weaker in germanosilicate zeolites. The structural degradation of germanosilicate takes place readily owing to the easy hydrolysis of Ge-O bonds, even by moisture under environmental conditions. The combination of these two factors provides the possibility for the preparation of layered zeolites from the already synthesized germanosilicates by exploiting chemically

selective weakness in 3D zeolite.⁸⁷ The treatment of 3D germanosilicates upon acid solution could induce the hydrolysis of Ge-rich D4R unit, which may eventually result in the collapse of 3D zeolite framework.¹⁵ Finally, the novel 2D zeolite with the layer the same as its corresponding 3D precursor is obtained. Therefore, a novel pathway for preparing layered zeolite could be performed through the hydrolysis process of 3D germanosilicate with the suitable structure and composition.

Based on this principle, Čejka and Roth *et al.* prepared a novel layered precursor IPC-1P from IM-12 zeolite with UTL structure in acid solution.¹⁵ The UTL topology can be viewed as a 3D zeolite structure constructed by linking the UTL layers with Ge-rich D4R units.⁸² Controlling the suitable hydrolysis conditions, the D4R can be completely removed, and the 2D layered zeolite is obtained by the stacking of the remaining UTL-like layers (Figure 10). However, this preparation should be delicately controlled, because the severe treatment upon Ge-rich UTL zeolite would give rise to highly stable siliceous zeolites with 3D structure through the isomorphous substitution of silicon for germanium.⁸⁸⁻⁸⁹ This “top-down” method is also applied to other D4R-containing germanosilicates with high Ge content.⁹⁰ Further NMR research indicated that the Ge atoms should be located in one of the faces of D4R units and form 4Rs that connect Si-rich layer together.⁹¹

The combination of regioselective location and hydrolytic sensitivity of Ge in germanosilicate could be used to develop the innovative preparation route for layered zeolites. However, as there is no active center involved in the germanosilicate framework, the catalytic application should be taken into account in the future.

3. Post-synthesis modifications of layered zeolites

As zeolites are essential as solid catalysts for oil refining, petrochemical processing and also organic synthesis, the sole presence of micropores often imposes significant limitations. By increasing the size of the pore opening, or by exposing the active sites that were originally inside the pores to the surface, reactants with large molecular dimension could gain access to the catalytic active centers more efficiently. Therefore, the importance of pore structure on the zeolite catalyst performance and the fact that a number of other zeolites are built from layered precursors led to the development of post-modification approaches with the purpose to maximize the surface chemistry of these materials. Various post-modification approaches have been developed to

achieve this goal, such as the swelling,⁴³ pillaring,⁴⁴ delamination,⁴⁵⁻⁴⁶ and interlayer silylation techniques (Figure 11).⁴⁷ The arrangement of zeolite layers in the resulting zeolites has been greatly changed, giving rise to a special family of hierarchical layered zeolites with higher accessibility. Compared with traditional zeolites obtained by direct calcination, the hierarchical structure enables zeolites to have maximum functions in a limited space owing to the high diffusion efficiency, which is more favorable for the catalytic conversion of large molecules.

3.1 Swelling, delamination and pillaring of layered zeolite

Generally, the breaking of the interaction and the expansion of the interlamellar space are required for the post-synthesis modifications of layered materials. The swelling process of layered precursor is usually carried out under severe conditions, such as high concentration of surfactant, strong alkaline solution and high temperatures, which has been successfully implemented in other layered materials, such as clay,⁹² metal oxides,⁹³ and other inorganic materials *etc.*⁹⁴

Although there is no covalently bonding between zeolite layers, but the hydrogen bonding and electrostatic interaction exist in layered zeolite. Therefore, it is not easy to break the strong interaction and then push the zeolite layers apart. The first realization of the swollen layered zeolite is on the MWW-type layered precursor MCM-22P.⁴³ The preparation process was initially carried out under severe conditions. The surfactant molecules were need to insert into the interlamellar space to support the neighboring layers as organic pillars. Specifically, the powder X-ray diffraction (PXRD) pattern of the swollen MWW zeolite shows the (001) reflection with a *d*-spacing > 5 nm and (003) reflection, while the (002) reflection is absent. Moreover, the integration of (101) and (102) reflections in the 2 theta range of 8 - 10 degree is another judgment of successful swelling.⁹ However, this treatment process should be delicately controlled to avoid the possibility of dissolving the layered precursor and subsequently self-assembling of siliceous mesophases. Besides, the severe treatment pays a negative impact on the chemical environment of catalytic activity center. Subsequently, a mild method was also proposed for the swelling of MCM-22P at room temperature.⁹⁵ The swollen material obtained by this method could be transformed reversibly into MCM-22P by acid treatment, while the zeolite framework preserved during the whole process. However, the treatment still needs high concentration of surfactants and strong basic medium. By using the similar method in the MCM-22P swelling, other layered precursors with

different structures were also achieved by the swelling, *e.g.* the layered precursor of FER,⁹⁶ NSI structure *etc.*⁹⁷

It is worth noting that the layered MFI zeolite could be regarded as the swelling type of layered zeolite, as the long-chain tails of bifunctional OSDA supporting the neighboring MFI zeolite layers, which is currently the only one instance directly obtained by hydrothermal synthesis.³⁹ Thus, a novel bifunctional catalytic system was developed based on this as-synthesized multilamellar MFI zeolites (Figure 12). Containing tripropyl head groups, the Gemini-type quaternary ammonium OSDA were firmly immobilized in the intersection of straight and sinusoidal 10-MR channels, with the other one exposed to the layer surface of the nanosheets. The existence of OSDA gave rise to two types of base sites, that is, the Lewis base sites due to the surface SiO^- species and Brønsted base sites due to the OH^- counteranion of exposed quaternary ammonium cations. A combination of the acid sites related to the framework Al and the base sites derived from coexisting OSDA endowed the catalysts with bifunctionalities useful in tandem catalysis.⁹⁸⁻⁹⁹

On the other hand, it can be deduced that the structure of swollen layered zeolite is not permanent, because the organic and inorganic alternative stacking is unstable. Thus, the swelling of MCM-22P is adopted as the first step to synthesize the pillared zeolite MCM-36 and the delaminated zeolite ITQ-2.⁴⁴⁻⁴⁵ The pillared zeolite material, in which the layers were supported each other with amorphous silica pillars, is prepared by treating the swollen layered precursor with TEOS and further remove the organic surfactants occluded between the interlayer space. The presence of silica pillars avoided the interlayer condensation during thermal calcination, resulting in a novel material with large interlayer spacing. The typical PXRD pattern of MCM-36 showed the (001) reflection with large *d*-spacing nearly the same as that of the swollen precursor.⁹ The 10-MR sinusoidal channels within MWW layers remain unchanged, while the other 10-MR channel and supercages are not formed after pillaring. But a new mesoporous cavities formed due to the interlayer separation by silica pillars. The typical pillared zeolites are MCM-36 (MWW),⁴⁴ ITQ-36 (FER),⁹⁶ MCM-39 (Si) (NSI)¹⁰⁰ *etc.*

The delamination process is to separate zeolite layers into single layers by various techniques. Typically, the pre-swelling process and the subsequent ultrasonic treatment were always combined to give the delaminated structure. Generally, the first step in the preparation of

delaminated layered zeolites is the swelling, because the interactions between the hydroxyl groups and the OSDA are weakened, as the distance between the layers in the swollen layered zeolite become larger. After the ultrasonic treatment of swollen layered precursor and the adjustment of the pH conditions, the delaminated layered zeolites were obtained. The delamination process could be tracked using PXRD patterns. As the MWW layers stacked irregular, the PXRD pattern of the delaminated ITQ-2 showed much weak (001) and (002) reflections, while the reflections in high angle region became broader for ITQ-2. The visible evidence of successful delamination could be observed from the HRTEM images, which showed the material was constructed by individual MWW layers with a random spatial distribution (Figure 13).⁴⁵ Recent studies also reported that tetrabutylammonium fluoride and tetrabutylammonium chloride were used to selectively interrupted Si-O-Si and Si-O-Al bonds, and then the delaminated layered zeolites can also be obtained under mild treatment conditions.¹⁰¹ Typical delaminated layered zeolites are ITQ-2,⁴⁵ UCB-1,¹⁰¹ and Del-Ti-MWW (MWW),¹⁰² ITQ-18 (NSI),⁹⁶ ITQ-6⁹⁷ and UCB-2 (FER)¹⁰³ *etc.* Obviously, the delaminated layered zeolites were the “real” two-dimensional zeolites. As the delaminated layered zeolite built with zeolite layers with single unit cell thickness, the diffusion limit in catalytic process was reduced to the lowest.

The delaminated layered zeolites could be used as catalysts in many reactions involved substrates with bulky molecular size. Since the catalytic active centers of the ITQ-2 and the MCM-36 zeolite are highly accessible, the superior performances of the exfoliated ITQ-2 were observed in the acid-catalyzed reactions, such as the cracking of vacuum oil and *n*-decane, and the dealkylation of 1,3,5-triisopropylbenzene. The catalytic performance of ITQ-2 in the reaction of vacuum oil cracking is superior to the conventional MCM-22 and MCM-36 zeolite. The yield of gasoline over ITQ-2 is much higher than that of the other two catalysts, while the yield of diesel oil is equal to MCM-36 zeolite.⁴⁵ Additionally, Pt species were supported onto the exfoliated MWW layers improved catalysts for hydrocracking of vacuum gas oil and aromatic hydrogenation.¹⁰⁴ The delamination technique was also applied on the layered precursor of titanosilicate, Ti-MWW-P, to produce the delaminated Del-Ti-MWW, which proved to be superior to TS-1, Ti-Beta, 3D Ti-MWW and even mesoporous Ti-MCM-41 in the epoxidation of a wide range of bulky alkenes with H₂O₂.¹⁰² Taking advantage of the high concentration of surface silanols, the organic active species were grafted

onto the individual MWW layers, resulting in organic-inorganic hybrid catalysts. The porphyrins and metaloporphyrins were incorporated onto the delaminated MWW layers for electrocatalyst for oxygen reduction processes. It was demonstrated that the delaminated ITQ-2 zeolite, maintaining the zeolitic acid strength, was more accessible catalysts for bulky molecules. The MCM-36 catalyst also exhibited a lower deactivation rate compared with the conventional MCM-22 catalyst in the conversion of methanol to hydrocarbons reaction.¹⁰⁵ Besides, the pillared MCM-36 is demonstrated to be highly active catalysts for chemical processes related to the *in situ* reduction of NO_x.¹⁰⁶

3.2 Partial delamination of layered zeolites

In addition to the full delamination of layered zeolite, a partial delaminated material, such as the MCM-56 analogue, was proposed and prepared by post-synthesis method over the 2D layered precursor.⁴⁶ Initially, MCM-56 used to be prepared by hydrothermal method with the same gel as MCM-22 but crystallized with shorter time, which cannot be well controlled. The post-synthesis method is a very convenient route including a mild acid treatment at low temperature and following calcination, whereas the acid treatment at elevated temperatures such as refluxing only resulting in conventional 3D MWW structure. The acid treatment induced partially detemplation and simultaneously lateral disorder. The material will be converted into MCM-56 analogue zeolite material after further calcination. Thus, the partial delaminated zeolite material is also called *Sub-zeolite*, which was assumed to be a collection of MWW monolayers, misalignment with possible coincidental cross linking. The formation of MCM-56 analogues was neither independent of the types of metallosilicates (containing B, Al, Ti, Ga or Fe ions) nor the amount of framework metal ions. Compared to the 3D crystal structure of MCM-22, the MCM-56 analogue has a relatively large external surface area, thus more catalytic activity centers are exposed. Heteratoms-containing MCM-56 (Ti, Sn, Al) analogue exhibited superior catalytic performance than conventional MWW zeolites in the catalytic process involved large molecules.^{46,107,108} The Ti-MCM-56 analogue was then superior to Ti-Beta, 3D Ti-MWW and TS-1 in the epoxidation of a wide range of bulky alkenes with *tert*-butyl hydroperoxide as well as in the oxidative desulfurization of dibenzothiophene with hydrogen peroxide. This method was successfully applied to the layered precursor of NSI and FER structure, giving rise to novel sub-zeolite ECNU-4 and ECNU-8, respectively.^{109,110}

3.3 Interlayer expansion through silylation

Typically, the layered precursor with OSDA molecules pillaring zeolite layers has an interlayer spacing in the range of 0.2 - 4 nm. The removal of OSDA molecules through calcination caused the condensation and dehydroxylation between the neighboring layers, resulting in a decreased layer spacing. Once 3D structure formed, the accessibility of bulky substrates to the active sites within channels is seriously restricted. The above described post-treatment techniques including swelling, delamination and pillaring are used to create more open reaction space. Besides, another type of interlayer expanded material could be constructed through the interlayer silylation with various monomeric Si species.

The layered zeolite with interlayer expanded structure was first discovered during the acid treatment process of Ti-MWW zeolite. Fan and Wu found that the acid-treated Ti-MWW showed slightly larger interlayer spacing along *c* axis than the 3D Ti-MWW and the layered precursor.¹¹¹ The combination of the analysis on PXRD data and HRTEM images indicated that this is due to the interlayer expansion of MWW structure.¹¹² A newly formed 12-MR that is distinct from the 10-MR of the MWW structure would explain this cell expansion (Figure 14). With the expanded pore window, which would result in a concomitant increase in steric accessibility, the Ti-YNU-1 catalyst showed significant enhancement of catalytic activity compared with other titanosilicates.¹¹¹ Inspired by the formation mechanism of Ti-YNU-1, Wu *et al.* developed a general methodology for expanding the interlayer structure of layered precursors of various topologies, such as MWW, FER, CDO, by postalkoxysilylation with diethoxydimethylsilane like $\text{SiMe}_2(\text{OEt})_2$ or SiMe_2Cl_2 under acidic conditions (Figure 15).⁴⁷ The silanes reacted with the silanol groups on the layer surface during the silylation process and then connected the layers to form an interlayer expanded structure. The interlayer expanded zeolites prepared from MWW precursors exhibited higher catalytic behaviors in the redox and solid acid-catalyzed reactions of bulky molecules than that of their counterparts with conventional MWW topology.¹¹³

The requirement of the above two methods of interlayer expansion is the acidic condition, in which the leaching of catalytic active sites was inevitably occurred. Tatsumi *et al.* developed a gas-phase silylation method, which not only realizes the expanding layered zeolite, and preserve the chemical environment of the active sites.¹¹⁴ By using the

interlayer silylation technique, various layered zeolite precursors have transformed into novel zeolites with larger interlayer channels, *e.g.* FER,¹¹⁵ Nu-6 (1),¹¹⁶ PLS-3,¹¹⁷ PLS-4,¹¹⁸ RUB-36,¹¹⁹ RUB-39¹²⁰ *etc.*

In addition to expand the layered precursor layers with single Si atom, recent studies have realized the expansion of interlayer opening with dimeric silane as pillars. The lamellar space is so small that the silane reagent cannot diffuse into the layer space. Therefore, the pre-swelling process was required to be carried out on the lamellar precursor, which created enough interlayer space for accommodating the dimeric silane molecules with a relatively large molecular dimension.¹²¹ The *d*-spacing of interlayer expanded MWW zeolite by dimeric silanes reached 30.9 Å, which is larger than that of the conventional 3D MWW (25.0 Å) as well as the silylated sample pillared by monomeric silane (27.5 Å). Besides, Corma *et al.* reported a novel layered zeolitic organic-inorganic materials (MWW-BTEB) by intercalation and silylation of aryl silsesquioxane molecules between the pre-swelling MWW zeolite layers.¹²² The obtained material contains micropores within the inorganic layers and well-defined mesoporous system in between the organic linkers, and it could be used as bifunctional catalyst for processing a cascade reaction. Similarly, a layered organic-inorganic zeolitic materials have been synthesized using the swollen-type layered precursor IPC-1SW. The generated materials contain organic linkers or polyhedral oligomeric siloxane covalently bonded to the zeolite layers in the interlayer space.¹²³

4. Structural interchange between layered zeolites

It is very interesting to explore the relationship between zeolites with various structures, and the construction of novel zeolite by linking the same zeolite layer differently. With the development of post-modification techniques, researchers have begun to study the possibility of the structural transformation between various layered zeolite.

As mentioned before, the novel 2D UTL layers could be prepared by the hydrolysis of 3D UTL zeolite with high Ge content through the “top-down” route. The Ge-rich D4R units could be selectively removed from the original UTL structure. Then, the resultant layers could be used as the building blocks of other topologies through the assembly-disassembly- organization-reassembly (ADOR) mechanism.¹²⁴ The UTL layers have been linked in two different ways to generate a family of zeolites structures with OKO and PCR topologies, in which the UTL layers linked with or without single 4-ring (S4R), respectively

(Figure 16).¹²⁴ The resulting IPC-2 zeolite is a medium/large pore material containing 10 and 12-MR, while IPC-4 is a small/medium pore zeolite with 8 and 10-MR. Recent studies have found that the zeolites with continuously tunable porosity were prepared by controlling the rates of two competing processes, silica deintercalation and reorganization, during the UTL hydrolysis process (Figure 17).¹²⁵ The reported IPC-6 contains two different layer spacings, 0.9 nm and 1.1 nm, which are nearly the same as that for the IPC-2 and IPC-4, respectively. The UTL layers in IPC-7 were expected to be linked by 50% D4R units and 50% S4R units, forming large pore opening with 14-MR and 12-MR. However, both of the materials should be regarded as disordered zeolites, not with intergrown structure. The precise control over layer stacking generates zeolite materials with continuously increasing surface area and microporosity, which provides the possibility of wide application of these materials. Recently, two new high-silica, IPC-9 and IPC-10, were prepared through the above-mentioned ADOR route.¹²⁶ Choline was adopted as the OSDA to induce the relative shift of UTL layers with respect to each other, forming in new zeolites with odd-membered rings. This results indicated that the zeolite layers may be acted as the building blocks to construct the novel 3D architecture with relative arrangement of the layers.

On the other hand, based on the fact that both the FER and CDO structures were constructed by the same ferrierite layer as building units, topotactic conversion from layered zeolite RUB-36 with CDO structure to ZSM-35 with FER structure has been demonstrated with the aid of a surfactant cetyltrimethylammonium hydroxide.¹²⁷

5. Perspectives

In recent years, great attention has been attracted in the field of layered materials, which have become an important subgroup of zeolite family. The direct synthesis of layered MFI precursor by specially-designed surfactants and the hydrolysis route from 3D gemanosilicates are innovative ways to 2D zeolites, which broaden the category of layered zeolite structure. With the development of the synthesis technology, the type of the layered zeolite is increasing. However, still very little is known about the growth process of the layered zeolite and the parameters controlling the layers stacking. Because crystallization of layered zeolites is a cooperative process where different reactions are occurring in a complex heterogeneous system. Each step of the synthesis process involves numerous simultaneous and

inter-independent equilibria and condensation steps. Therefore, a detailed understanding of layered zeolite growth is highly desirable in order to control the synthesis of this type of materials.

On the other hand, the structure modification of layered zeolites produced many novel hierarchical materials, which may turn out to be catalytic promising catalysts for petrochemical industry. However, the postsynthetic modification may be carried out through more green and moderate routes. Additionally, the direct hydrothermal synthesis of hierarchical catalysts with zeolite layers disordered stacking is also an attractive area, such as recently developed layered MFI zeolites, which could be regarded as the swelling type of layered zeolite. The direct synthesis of functional layered zeolites would avoid the existing complex post-modification processes. The layered zeolite has shown superior catalytic performance to the traditional 3D zeolite in the production of a variety of petrochemical and fine chemicals, therefore exploring their catalytic performance is another promising research direction in future study.

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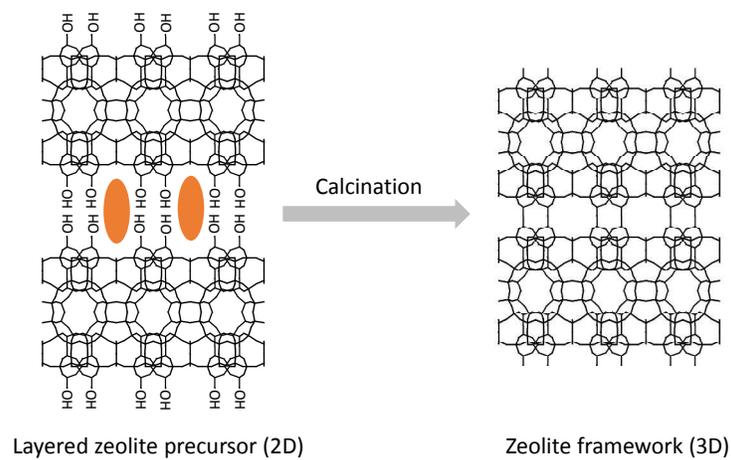


Figure 1. Schematic description of structural transformation from layered precursor to 3D topology with MWW zeolite as a representative example.

Table 1. List of existed layered zeolites.

Layered zeolites	Structure code	Pore size	Reference
MCM-22	MWW	10*10 MR	[17]
SSZ-25	MWW		[18]
PSH-3	MWW		[19]
ERB-1P	MWW		[20]
ITQ-1P	MWW		[21]
Ti-MWW-P	MWW		[22-23]
SSZ-70	unknown	-	[24]
EMM-10P	unknown	-	[25]
PREFER	FER	10*8 MR	[26]
PLS-3	FER		[27]
MCM-47	FER/CDO	-	[28]
MCM-65	CDO	8* 8 MR	[29]
PLS-1	CDO		[30]
PLS-4	CDO		[27]
EU-19	CAS	8 MR	[31]
MCM-69	CAS		[32]
Nu-6(1)	NSI	8 MR	[33]
RUB-15	SOD	6 MR	[34]
RUB-18	RWR	8//8 MR	[35]
RUB-51	RWR	8//8 MR	[36]
RUB-39	RRO	10*8 MR	[37]
PreAFO	AFO	10 MR	[38]
Layered MFI	MFI	10*10 MR	[39]
IPC-1P	PCR	10*8 MR	[15]
HPM-2	MTF	8 MR	[40]
CIT-10	RTH	8*8	[41]
HUS-2	unknown	-	[42]
HUS-3	unknown	-	[42]

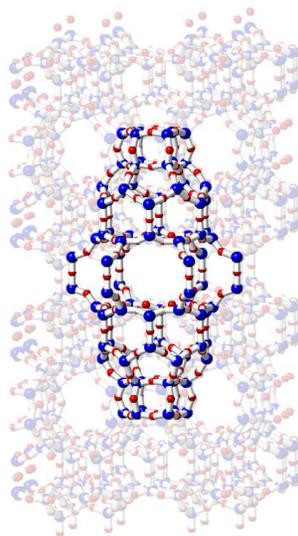


Figure 2. Description of MWW supercages.

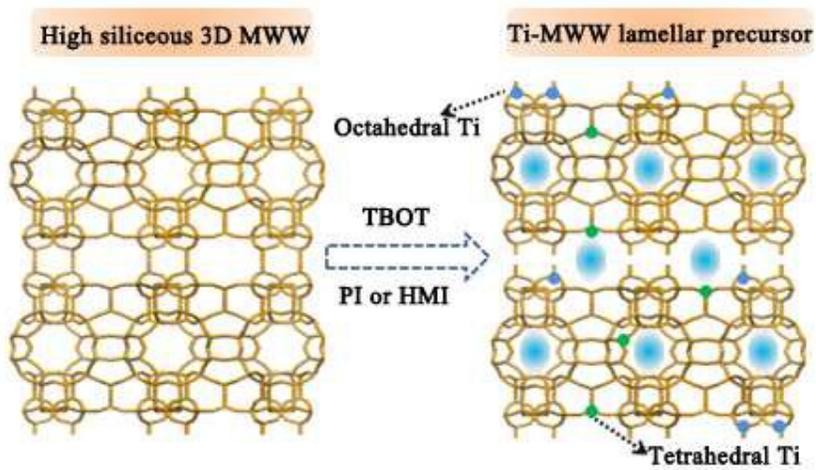


Figure 3. Graphic description for the postsynthesis of boron-free Ti-MWW through reversible structure conversion.

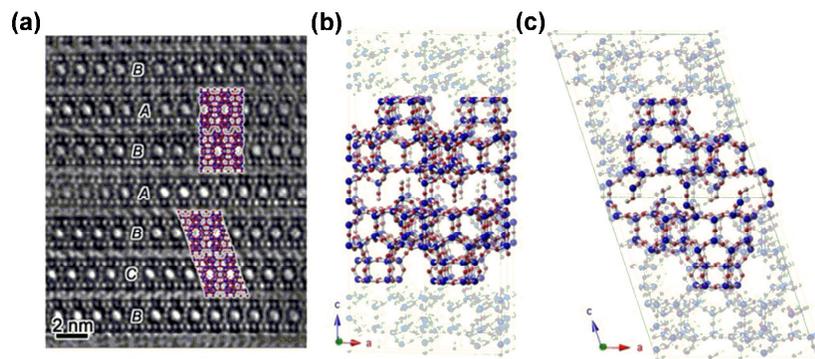


Figure 4. (a) HRTEM image of ECNU-5 with intergrown MWW structures. Structural model of (b) ECNU-5A and (c) ECNU-5B.

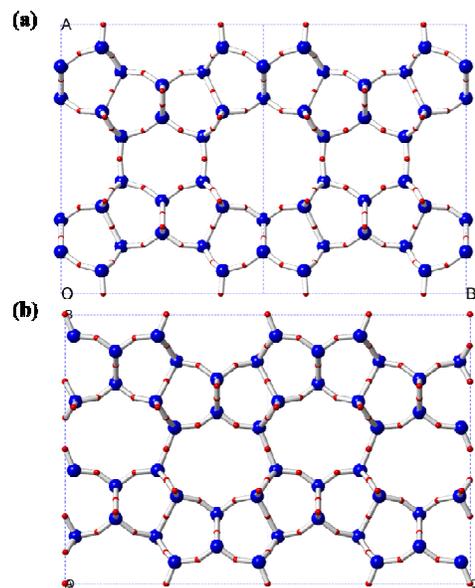


Figure 5. Structure model of (a) FER and (b) CDO, both of which were composed of ferrierite layer.

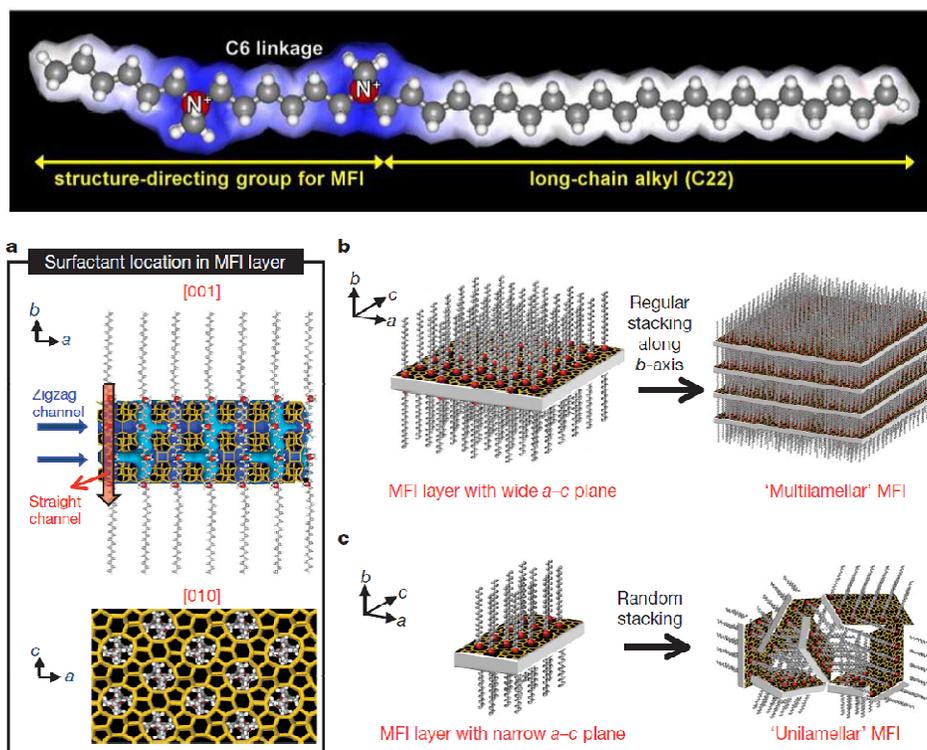


Figure 6. Graphic description for the synthesis of layered MFI nanosheet. Copyright 2009, with permission from Nature Publishing Group.

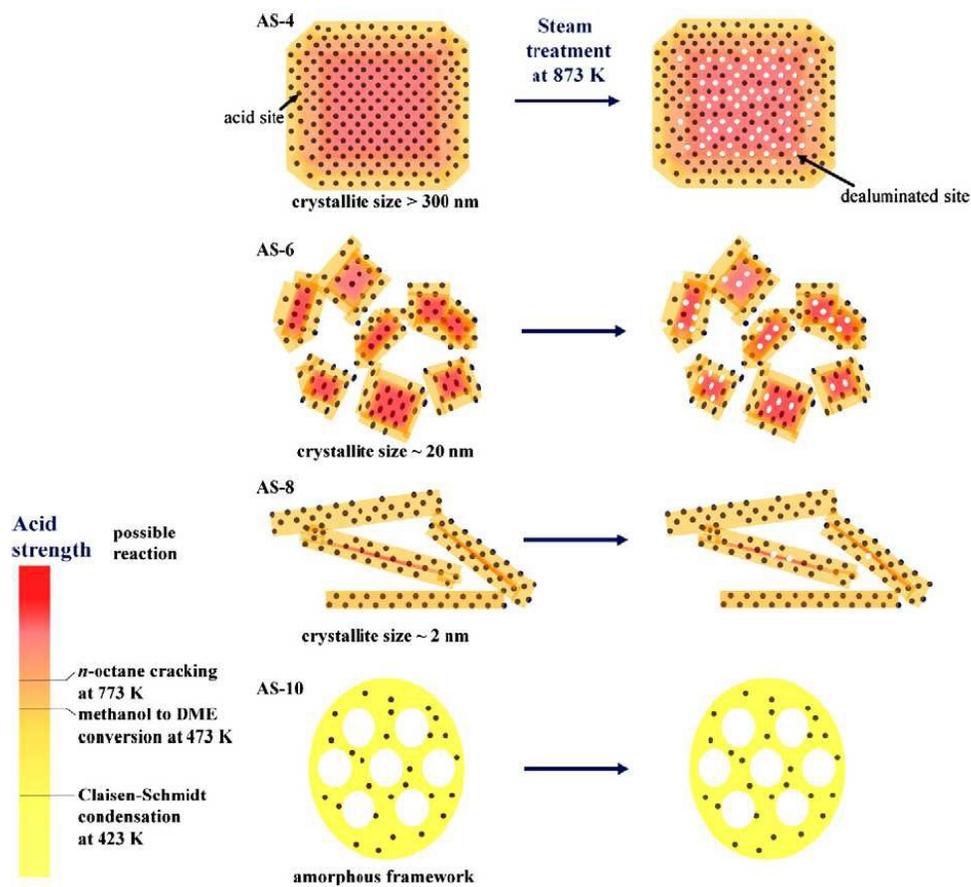


Figure 7. Schematic description of the spatial distribution, strength, and steam stability of the acid sites in the aluminosilicate. Copyright 2012, with permission from Elsevier.

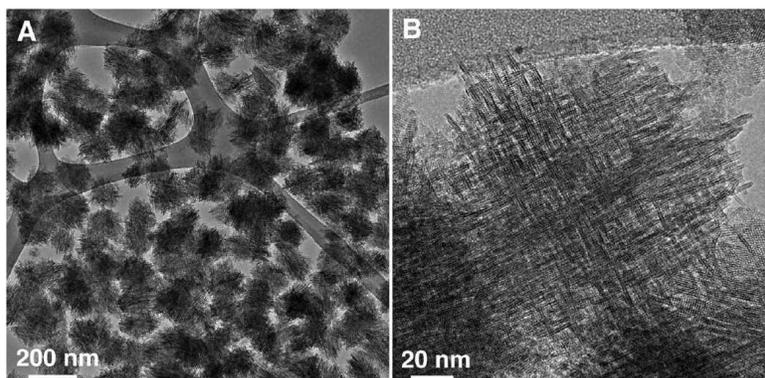


Figure 8. HRTEM images of self-pillared MFI zeolite nanosheets. Copyright 2012, with permission the American Association for the Advancement of Science.

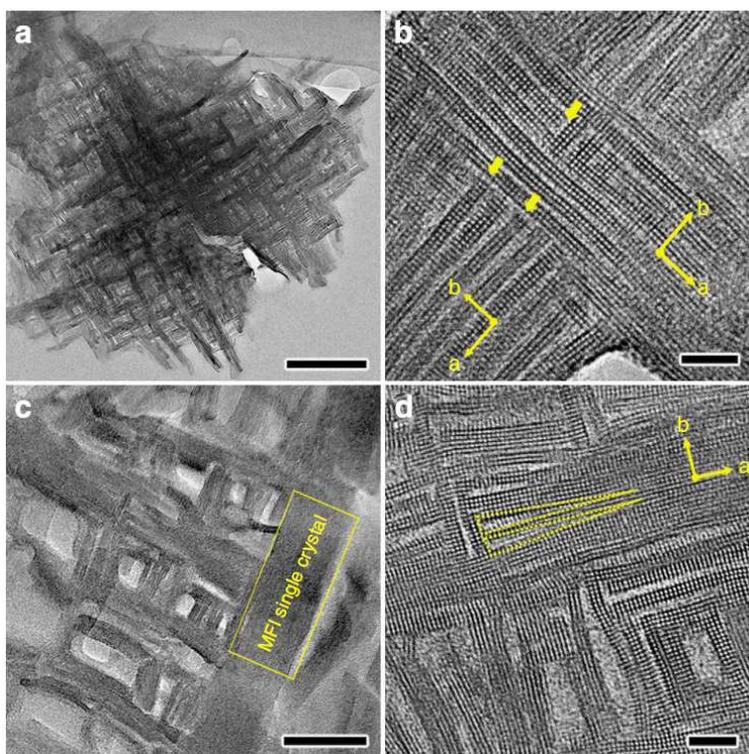


Figure 9. HRTEM images of as made (a, b) and calcined hierarchical MFI zeolite (c, d). The scale bars in a, b, c, d represent 200 nm, 10 nm, 50 nm and 10 nm, respectively. Copyright 2014, with permission from Nature Publishing Group.

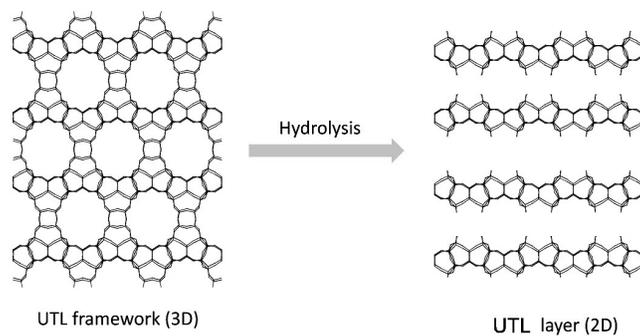


Figure 10. Schematic description of the hydrolysis of UTL zeolite.

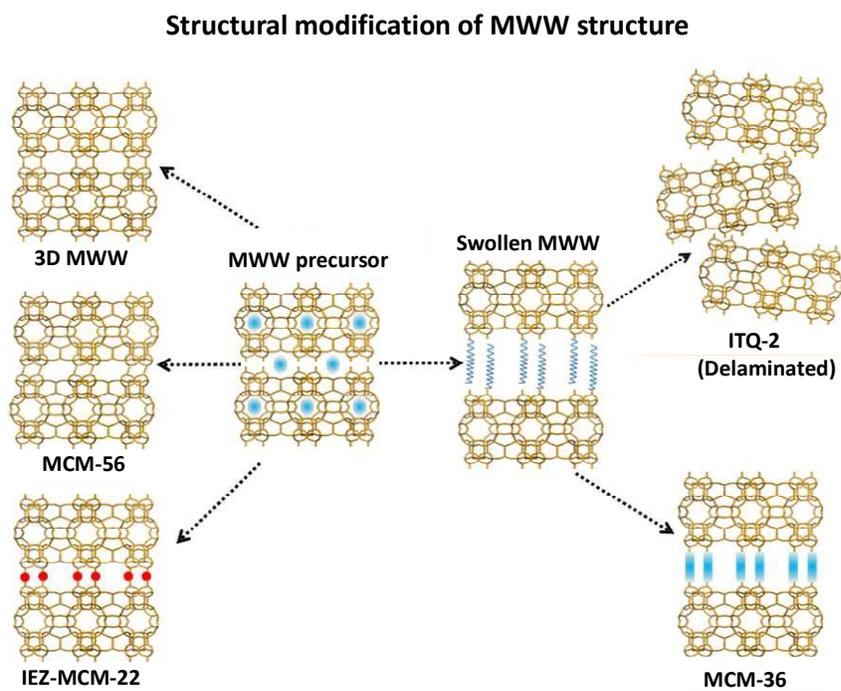


Figure 11. Scheme of structural modification of MWW layered precursor.

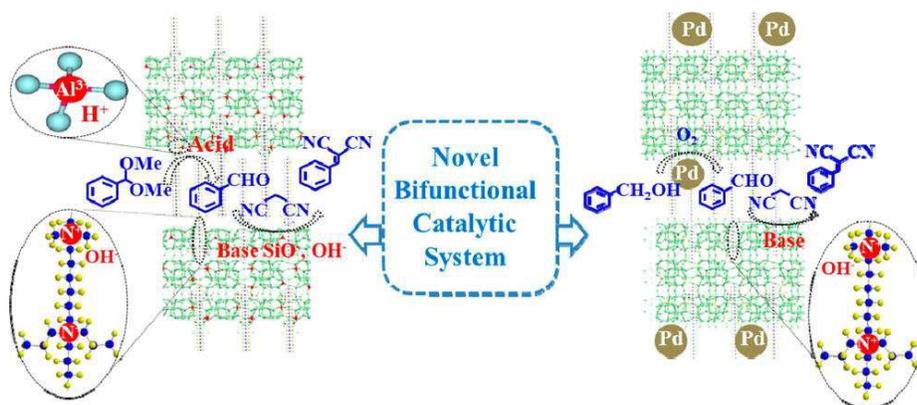


Figure 12. Illustration of bifunctional catalytic system based on as-synthesized layered MFI zeolites. Copyright 2014, with permission from American Chemical Society.

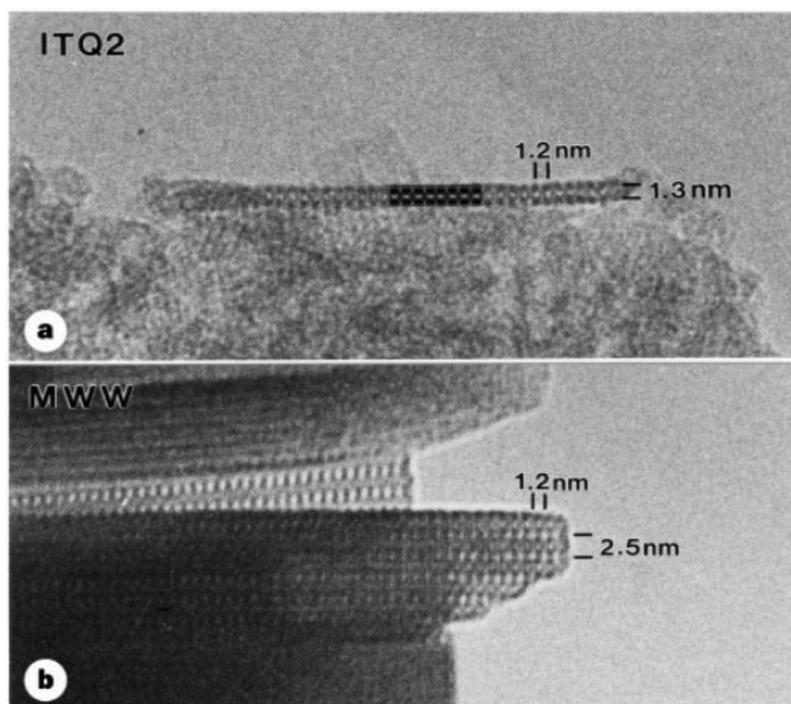


Figure 13. HRTEM images of the delaminated MWW zeolite ITQ-1 (a) and the conventional MWW zeolite MCM-22 (b). Copyright 1998, with permission from Nature Publishing Group.

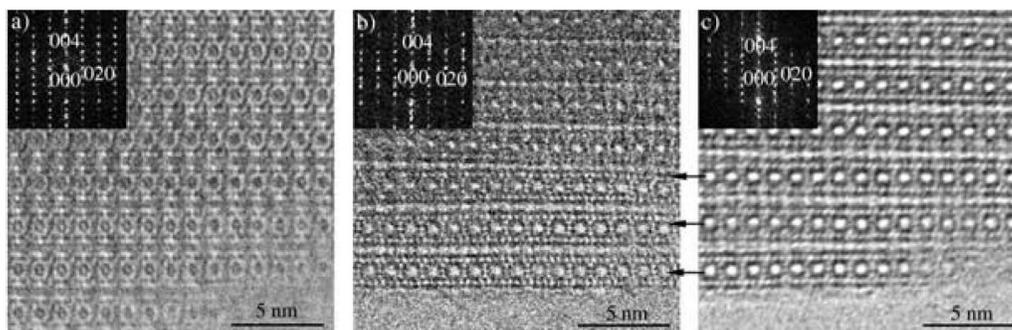


Figure 14. HRTEM images of the conventional 2D Ti-MWW precursor (a), 3D Ti-MWW (b) and the interlayer-expanded zeolite Ti-YNU-1 (c). Copyright 2005, with permission from Wiley-VCH Verlag GmbH & Co. KGaA.

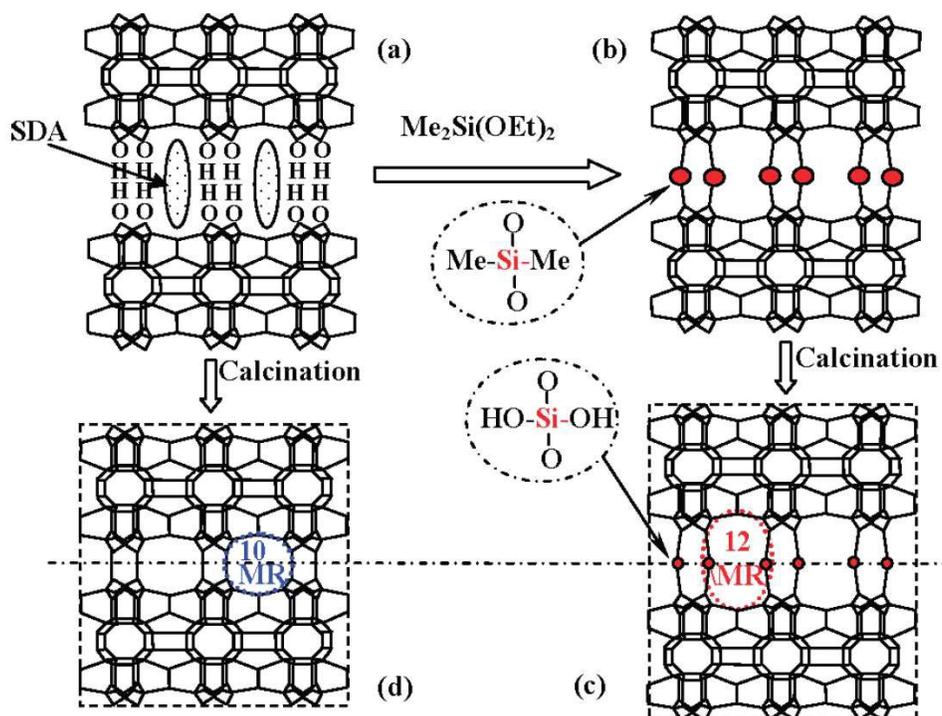


Figure 15. Schematic description of the process of interlayer silylation technique. Copyright 2008, with permission from American Chemical Society.

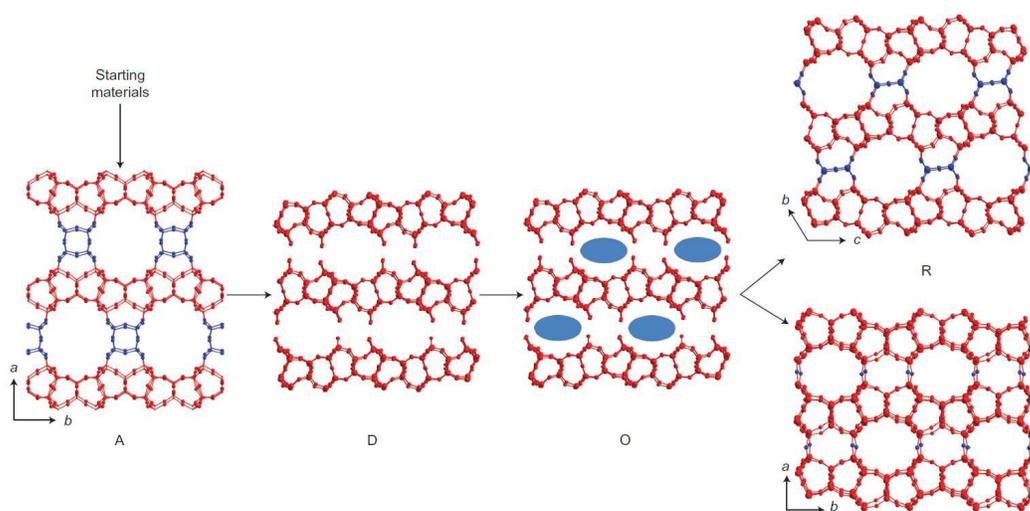


Figure 16. Illustration of the assembly-disassembly-organization-reassembly (ADOR) process. Copyright 2013, with permission from Nature Publishing Group.

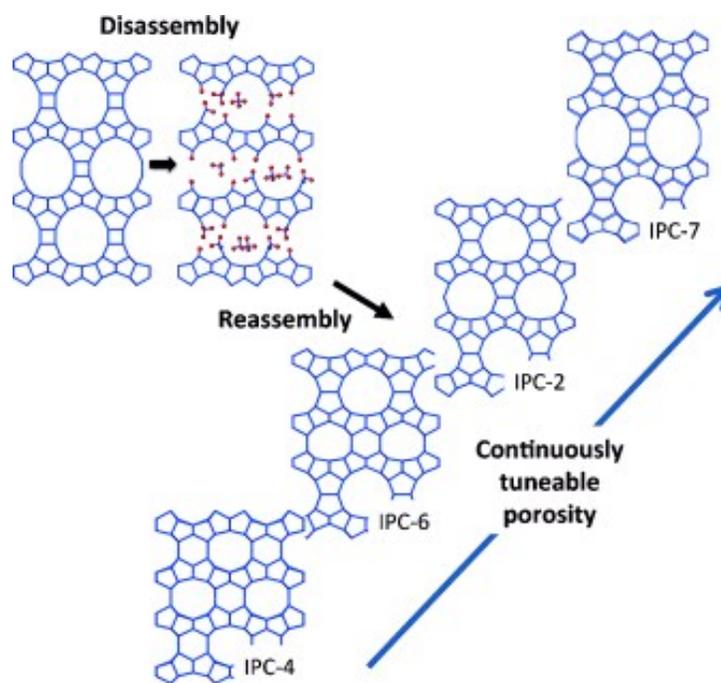
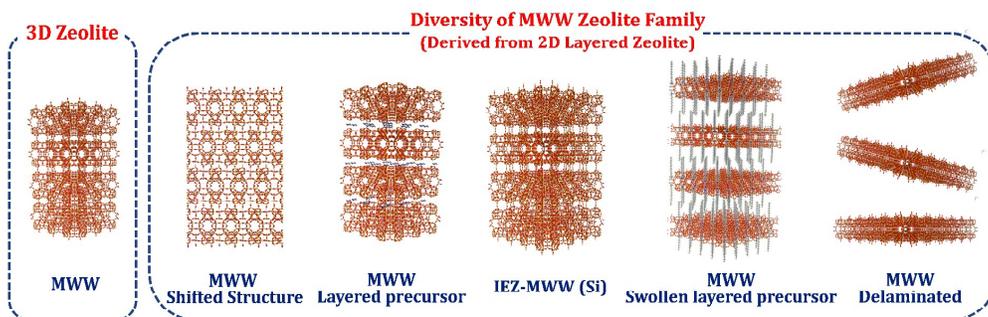


Figure 17. Description of different stages of ADOR process from 3D UTL zeolite. Copyright 2014, with permission from Wiley-VCH Verlag GmbH & Co. KGaA.

Graphic abstract:



The most attractive achievements in the research area of layered zeolites are summarized, including synthesis, modifications strategies and catalytic applications. The challenges for future researches on this type of porous materials are also proposed.