Chapter

New Trends in Layered Zeolites

Hao Xu and Peng Wu

Abstract

Layered zeolites, with a flexible and changeable interlayer connection, can be modified to give a great number of derivative structures with enlarged pore sizes or enhanced external surface areas, via swelling, delamination, pillaring, or silylation. In recent years, great efforts have been devoted to the synthesis of novel-layered zeolite precursors, by using the specially designed bifunctional amphiphilic surfactants as the structure-directing agents or through the selective degradation of double four ring-containing germanosilicates. In addition, the novel modifications, such as mild delamination, interlayer expansion assisted by deconstruction-reconstruction, and layer-stacking reorganization by dissolution-recrystallization, have also been developed to create more derivatives while achieving better preservation of layer structures. Recent progresses in the field of layered zeolites are summarized in this chapter, and the challenges for future development are also proposed.

Keywords: layered zeolite, design synthesis, structural modification, delamination, interlayer expansion

1. Introduction

Zeolites, with high-crystalline three-dimensional (3D) frameworks composed of TO$_4$ (T = Si or Al, etc.) tetrahedrons, have found their unique advantages in the field of adsorption, separation, and catalysis, owing to a large surface area, uniform pore channels of molecular size, strong acidity, and redox ability. According to the International Zeolite Association (IZA), 244 kinds of zeolites have been recognized up to date, most of which are hydrothermally synthesized [1]. In addition, the topotactic conversion from two-dimensional (2D) lamellar precursors to 3D rigid zeolite framework contributes ~10% of the whole zeolite family [2]. Rather than strong and rigid covalent bonds, relative weak and flexible hydrogen bonds are the interaction force between the neighboring layers in 2D lamellar precursors, which are also called layered zeolites. These hydrogen bonds are derived from the abundant silanol groups on the layer surface, which would condense to form Si–O–Si linkage upon calcination and then produce 3D zeolite frameworks.

In the very beginning, layered zeolites are occasionally obtained from the traditional synthetic gels that were designed to produce 3D zeolites. However, the formation mechanism of these layered zeolites is still a mystery, which prohibits the researchers to design and synthesize more novel-layered zeolites via the traditional hydrothermal synthesis. Recently, several novel strategies have been proposed to synthesize layered zeolite, including the usage of specially designed bifunctional structure-directing agents (SDA) [3] and the transformation of 3D germanosilicates to 2D lamellar zeolites by posttreatment [4]. The newly established methods expanded the layered zeolite family, and there are now nearly 30 kinds of layered zeolites available (Table 1).
The interlayer flexible hydrogen bonds endowed the layered zeolites with modifiable structural property. Post-modifications including swelling [29], delamination [30, 31], pillaring [32], silylation [33], and detemplating [34] have been reported to increase the interlayer space or to gain higher external surface area (Figure 1). The classical swelling process is achieved by the intercalation of layered zeolites with large-sized surfactant molecules in the alkaline organic ammonium solution, resulting in enlarged interlayer space [29]. An ultrasonic treatment over the swollen intermediate produces full delaminated materials, changing the original ordered stacking style to house-of-cards arrangement and greatly enhancing the external surface area [30, 31]. Again, based on the swollen intermediate, the enhanced interlayer space can be stabilized by rigid silica pillars, giving pillaring materials with interlayer mesopores and intralayer micropores [32]. In contrast, interlayer silylation is an atom-level accurate modification to produce interlayer-expanded structures [33]. Detemplating, including the full and partial removal of the interlayer SDA molecules, results in a 3D zeolite framework and partial delaminated

| Layered precursors | Structure code* | Main pores for 3D structure | Reference |
|--------------------|-----------------|----------------------------|-----------|
| MCM-22             | MWW             | 10 × 10-R, 12R cages       | [5]       |
| PSH-3              |                 |                            | [6]       |
| SSZ-25             |                 |                            | [7]       |
| ITQ-1              |                 |                            | [8]       |
| ERB-1              |                 |                            | [9]       |
| EMM-10             |                 |                            | [10]      |
| SSZ-70             |                 |                            | [11]      |
| ECNU-5             |                 |                            | [12]      |
| PREFER             | FER             | 10 × 8-R                   | [13]      |
| PLS-3              |                 |                            | [14]      |
| MCM-47             | CDO             | 8 × 8-R                    | [15]      |
| MCM-65             |                 |                            | [16]      |
| PLS-1              |                 |                            | [17]      |
| PLS-4              |                 |                            | [14]      |
| RUB-36             |                 |                            | [18]      |
| EU-19              | CAS             | 8R                         | [19]      |
| Nu-6(1)            | NSI             | 8 × 8-R                    | [20]      |
| RUB-15             | SOD             | 6R                         | [21]      |
| RUB-18             | RWR             | 8 × 8-R                    | [22]      |
| RUB-39             | RRO             | 10 × 8-R                   | [23]      |
| PreAFO             | AFO             | 10R                        | [24]      |
| Lamellar MFI       | MFI             | 10 × 10-R                  | [3]       |
| IPC-1P             | PCR             | 10 × 8-R                   | [4]       |
|                    |                 | *PCS 12 × 10-R, 10 × 8-R   | [25]      |
| ECNU-21P           |                 | 10 × 6-R                   | [26]      |
| MCM-69(P)          |                 |                            | [27]      |
| HUS-2              |                 |                            | [28]      |

*The structure code for the 3D zeolite obtained from layered precursor upon calcination.

Table 1.
Listing of existing layered zeolite.
materials, respectively [34]. Although these posttreatments have achieved a great success for most of the layered zeolites, the corrosion effect of the alkaline solution on intralayer structure in swelling process, the multistep procedure of delamination, and the failure of silylation over some special layered zeolites cannot be ignored, and new modification strategies are highly desired.

This chapter will review the recently developed synthetic methods, including the usage of bifunctional surfactants and the selective degradation of germanosilicates, and the modification strategies of layered zeolites, such as mild delamination, interlayer expansion assisted by deconstruction-reconstruction, and layer-stacking reorganization by dissolution-recrystallization. One of the most important driving forces of novel-layered zeolite exploration and modification improvement is to design synthesis of more efficient catalysts, with better accessibility of active sites provided by enlarged pores and external surface areas. Thus, this chapter will also cover the catalytic performance of the newly developed layered zeolite and derivative materials in the solid acid/base-catalyzed reactions and the liquid selective oxidation reactions. For the conventional synthesis, characterization, classical modifications, and applications of layered zeolites, the readers could find them in the published reviews [35–40]. In the end, the challenge and possible future development in the field of layered zeolites is prospected.

2. Newly developed synthetic methods

2.1 Synthesis of layered zeolites with bifunctional amphiphilic SDAs

Compared to the continuous expanding in the 3D directions for typical zeolite frameworks, the layered structures only spread in 2D directions, with the growth in

Figure 1. Summary of the post-synthesis modifications over a typical MWW lamellar zeolite.
the third direction being interrupted. Considering this unique structural property of layered zeolites, Ryoo et al. proposed a novel strategy to synthesize layered zeolites using specially designed bifunctional amphiphilic SDAs with the hydrophilic diquaternary ammonium head to direct the crystallization of intralayer structures and on the other hand the hydrophobic long alkyl chain to prevent the continuous growth in the direction vertical to the layers [3, 41]. MFI-layered zeolite, hardly obtained in the traditional hydrothermal synthesis, was firstly reported using this method with the surfactant of \(C_{22}H_{45}^+\)(CH\(_3\))\(_2^+\)\(\cdot\)\(C_6H_13\)\(\cdot\)\(N^+\)(CH\(_3\))\(_2^+\)(CH\(_3\))\(_2^+\)\(\cdot\)\(C_6H_{13}^-\). A large amount of Na\(^+\) in the synthetic gel favored the alternating stacking of 2-nm-thick MFI nanosheets and 2.8-nm-thick surfactant micelles, producing multilamellar MFI with an overall thickness of 30–40 nm (Figure 2A–D). However, reducing the Na\(^+\) resulted in the formation of unilamellar MFI nanosheets (Figure 2E). Both of the two-layered MFI zeolites exhibited a significantly higher surface area than that of the traditional 3D MFI zeolite, due to the formation of mesopores upon calcination. The layered MFI zeolites showed longer lifetime in the methanol-to-gasoline reaction and higher catalytic activity in the reactions involving large-size molecules, due to the simultaneous presence of mesopores and micropores. Similar superior catalytic results were reported by comparing the performance of layered TS-1 zeolite to that of bulk TS-1 in the epoxidation reactions [42]. The as-synthesized multilamellar MFI zeolite has also been applied as an acid-base bifunctional catalyst in the Knoevenagel condensation reactions. The acid site was derived from the Al-related Brønsted acidity, while the ammonium group located in the pore mouth served as a base site [43].

The structure of the bifunctional amphiphilic SDAs was then proved to be critical for the synthesis of layered MFI zeolite [44]. Too small space between the two ammonium groups would result in bulk MFI, while too large space leads to the disordered stacking of MFI nanosheets. Tuning the number of ammonium group is effective in controlling the thickness of MFI nanosheets. The hydrophobic alkyl chain should be long enough to form a micellar structure. Once two long alkyl chains were present in the bifunctional SDA, hexagonal mesostructure was formed with the pore wall characterized with crystalline MFI structure having the thickness of 1.7 nm [45]. By introducing aromatic groups into the hydrophobic chain of bifunctional SDA molecules, Che et al. have synthesized several lamellar MFI zeolites with different mesostructures, benefiting from the strong \(\pi\)-\(\pi\) stacking and the geometrical match between aromatic groups and MFI zeolitic frameworks [46–48]. This strategy of using bifunctional SDAs has been successfully extended to

![Figure 2. SEM (A) and TEM (B) images of layered MFI zeolite. The scheme for the single layer MFI nanosheet (C) and the structural model for multilamellar MFI (D) and unilamellar MFI (E).]
the synthesis of nanosheets with MTW [3], *MRE [49], and AlPO [50] frameworks, which have never been synthesized as 2D zeolites before.

For the well-known MWW-layered zeolite, a bifunctional SDA with the head group resembling the SDA for conventional MWW-layered zeolite and a long alkyl chain connected by diquaternary ammonium linker directed the crystallization of MIT-1 composed of MWW nanosheets with a house-of-cards arrangement (Figure 3), which was similar to the delaminated MWW material [51]. MIT-1 exhibited high mesoporosity with the external surface area higher than that of MCM-56 but lower than ITQ-2. This one-pot synthetic method using rational designed bifunctional SDA to prepare delaminated material avoids the conventional multistep process and also the amorphization of layer structure in the swelling treatment. Another directly synthesized delaminated MWW zeolite, DS-ITQ-2, was reported by Corma et al., under the co-directing effect of hexamethyleneimine (HMI) and a bifunctional SDA of N-hexadecyl-N’-methyl-DABCO (C_{16}DC_{i}) [52]. HMI, the traditional template for the crystallization of layered MWW zeolite, was applied to direct the crystallization of MWW layers. For the bifunctional SDA, the hydrophilic head is located in the pocket of MWW layers, while the long hydrophobic chain prevents the ordering of stacking along c axis. The obtained DS-ITQ-2 showed a comparable catalytic activity as the conventional delaminated material of ITQ-2 in the liquid phase alkylation of benzene with propene.

2.2 Synthesis of layered zeolites by selective removal of double four rings from germanosilicates

Germanosilicates, with novel topologies and large-pore channels, have shown their great potential in the catalytic reactions involving bulky substrates. Ge atoms favored the formation of double four ring (D4R) and double three ring (D3R) when building the zeolite frameworks together with silica atoms, due to their longer
Ge—O bond and smaller Ge—O—Ge bond angle. Then, it is easy for these D4R and D3R subunits to construct large or extra-large pore channels, such as ITQ-37 (30R) [53], ITQ-43 (28R) [54], ITQ-44 (16R) [55], etc. However, the instability of Si(Ge)—O—Ge bonds prevents the practical applications of germanosilicates. On the bright side, the instability of germanosilicates endowed them structural modifiable properties. Taking full advantage of this, Čejka et al. have put forward an effective strategy, called the assembly-disassembly-organization-reassembly (ADOR), to transform the 3D zeolite frameworks to 2D layered zeolite by selectively removing the Ge-rich D4R subunits in UTL germanosilicate under acidic environment to give IPC-1P lamellar intermediate (Figure 4) [4]. The obtained lamellar zeolite was then organized and reassembled by organic amine treatment, calcination, or interlayer silylation, giving a series of novel zeolite frameworks (IPC-\(n\)) [56–58]. Three of these novel UTL-derived zeolites, including OKO [59], PCR [4], and *PCS [25], have been recognized by the IZA structure committee. The alternating stable Si-rich zeolitic layer and instable Ge-rich D4R subunits and high Ge content are the key

Figure 4.
Scheme description of ADOR strategy to create layered zeolite intermediates under acidic condition and novel germanosilicate derivatives.

Figure 5.
Selective hydrolysis of germanosilicates CIT-13 under alkaline medium to give layered zeolite ECNU-21P.
factors for the successful structural transformation. The ADOR strategy assisted by an acidic solution has been successfully extended to other germanosilicates, including ITH, IWR [60], IWW [61], UOV [62], and SAZ-1 [63].

Although CIT-13 germanosilicate meets all the criteria for ADOR strategy, it failed to give any lamellar zeolite. More detailed characterization indicated that the presence of Si–O–Si bonds vertical to the Si-rich layers may prohibit the successful selective removal of D4R subunits [64]. Wu et al. reported a mild alkaline treatment to hydrolyze both Ge–O–Ge(Si) and Si–O–Si bonds in the D4R subunits, giving a layered intermediate ECNU-21P (Figure 5), which was transformed to 3D ECNU-21 zeolite upon calcination [26]. In addition, the selective removal of D4R subunits from CIT-13 zeolite eliminates the intergrowth phenomena and resulted in a single crystalline zeolite framework. The alkaline medium-assisted ADOR strategy works as a good addition to the original acid system and is expected to create more layered zeolites.

3. Novel modification strategies

3.1 Delamination of layered zeolite under mild conditions

The conventional delamination process includes the swelling process and a subsequent ultrasound treatment in alkaline solution with the typical pH value of ~13, which causes severe dissolution of the intralayer structures [30, 31]. Moreover, the mesoporous phase formed form dissolved silica species in swelling process, like MCM-41, may also contribute to the high surface area, which could give cheating information for the success delamination. Zones and Katz reported a delaminated MWW zeolite synthesized under mild condition, where a solution of tetrabutylammonium fluoride and chloride surfactants with a pH value of 9 was used (Figure 6) [65]. The fluoride ion could form a strong interaction with Si atoms, while the chloride ions would attack Al atoms in the delamination process. High solid yield of ~90% was obtained under the mild condition compared to the yield of ~75% under classical alkaline condition with the same treatment temperature and duration. The successful delamination was strongly evidenced by the loss of interlayer 10R pores, characterized by the decrease of the N₂ uptake in the relative pressure of 10⁻⁷ < p/p₀ < 10⁻⁴. The absence of Q² signals and the sharper Q⁴ resonance bands in the ²⁹Si NMR spectrum of delaminated UCB-1 material strongly indicated that the intralayer structure was well-preserved under the mild condition. However, a nonaqueous fluoride/chloride solution was needed in the delamination of the PREFER lamellar zeolite, and dimethylformamide was proved to be a suitable solvent in producing the delaminated UCB-2 material [66].

Figure 6.
Mild delamination of MWW-layered zeolite with the assistance of F⁻ and Cl⁻ ions.
A more simple and mild delamination strategy without surfactant molecules and sonication was also proposed by Zones and Katz via the isomorphous substitution of Al for B in the B-containing MWW zeolite using aqueous Al(NO$_3$)$_3$ solution (Figure 7) [67]. The presence of neutral amine SDA and the careful control of temperature were proved to be critical for the success of this one-step delamination process. The obtained delaminated Al-containing ERB-1-del showed a similar morphology of single thin layers as the conventional delaminated ITQ-2 material and showed higher activity in Friedel-Crafts acylation reactions involving bulky substrates compared to 3D ERB-1C zeolite, due to the enhanced external surface area (133 vs 53 m$^2$/g). An all-silica analog of ERB-1-del can be obtained by treating ERB-1 lamellar precursor with warm Zn(NO$_3$)$_2$ solution with a pH value of ~1 [68]. However, the one-step mild delamination strategy is now restricted to ERB-1 lamellar precursor and has its limitations in the general application.

3.2 Interlayer expansion with large-sized silane agents assisted by deconstruction-reconstruction

Although the simple high-temperature acid treatment is able to give interlayer-expanded structures, the assistant of silane agents helps the formation of more ordered and stable structures [69, 70]. The interlayer space of most lamellar precursors is large enough for monomolecular silane agent to insert two additional Si atoms in the pore window. To introduce more Si atoms and construct larger interlayer pore structures, the interlayer silylation achieved by large-sized silane molecules should be performed over the swollen intermediate [71, 72]. However, the conventional swelling process under the basic condition induces severe amorphization of the layer structures. To tailor the interlayer space, an interlayer deconstruction-reconstruction strategy was proposed by Wu et al. [73]. The PLS-3 lamellar precursor was firstly deconstructed by a mild acid treatment to induce the partial removal of SDA molecules and then reconstructed in the aqueous solution.
containing bulky ammonium molecules, resulting in a lamellar precursor ECNU-9(P) with an enlarged interlayer space (Figure 8). The bulky ammonium molecules are the classical SDA for the PREFER-layered zeolite having the same layer structure as PLS-3. Thus, the layer structure of PLS-3 was well-protected in the reconstruction process. The interlayer-expanded ECNU-9 zeolite with large/extra-large pore system of 14 × 12-R was synthesized by the intercalation of a bulky single four ring-shaped silane agent into ECNU-9(P). Ti-ECNU-9, obtained by incorporating Ti atoms into ECNU-9 via H₂TiF₆ treatment, exhibited significantly high activity in the epoxidation reaction of cyclohexene, compared with 3D Ti-FER and the one expanded by monomolecular silane agent.

A similar strategy was also reported in the silylation of HUS-2-layered zeolite [74]. A distance of a half unit cell along [001] the direction for the up-and-down silanols on the layer surface and the presence of silicon vacancy induced the structural collapse of HUS-2 upon calcination [28]. Thus, a dimeric silane agent with two active groups attached to each silicon atom was applied to connect the relative long-distance up-and-down silanols and simultaneously fill the vacancy. The original HUS-2 lamellar zeolite could not offer enough interlayer space to accommodate the bulky dimeric silane agent. Thus, a Sub-HUS-2 material with interlayer deconstructed structure was firstly prepared and then reconstructed with the assistance of bulky ammonium molecules, resulting in an enlarged interlayer space for the following silylation. The obtained interlayer-expanded ECNU-19 zeolite with intersecting 12 × 8-R pore system was confirmed by the structure refinement.

Figure 8.
Scheme description of interlayer-expanded ECNU-9 zeolite via deconstruction-reconstruction strategy.
3.3 Reorganization of layer stacking by rapid dissolution-recrystallization method

The reorganization of layer-stacking style is a useful strategy to produce partial delaminated materials, which preserved more micropores compared to full delaminated ones [34, 75]. Although the delaminated analogs can be obtained by direct hydrothermal synthesis [10, 76, 77], the posttreatment modification is easier to control. Partial detemplating by a mild acid treatment over MWW-layered zeolite produced MCM-56 with higher external surface area than conventional 3D MWW zeolite [34, 75]. In addition to this, a novel strategy of rapid dissolution-recrystallization was reported to give an intergrowth ECNU-5 zeolite with two different polymorphs of ECNU-5A and ECNU-5B (Figure 9) [12]. In the SDA-containing alkaline solution, the 3D all-silica MWW precursor ITQ-1 was fast dissolved to silica species in 1 h, which were then recrystallized to a lamellar material ECNU-5P with the assistant of the unique SDA of 1,3-bis(cyclohexyl) imidazolium hydroxide. The asymmetrical cyclohexyl groups in the SDA molecule were responsible for the disordered stacking style and the resultant intergrowth structure by geometry mismatching. A new pore window with the size close to 14R was found in the ECNU-5 zeolite, different from the 12R cage in the traditional 3D MWW because of the misconnection of the up-and-down pockets from neighboring layers. ECNU-5 zeolite was later proved to be analogous to SSZ-70 zeolite [11, 77].

A direct synthesized swollen MWW material ECNU-7P can be obtained by introducing the surfactant of cetyltrimethylammonium bromide (CTAB) in the above recrystallization process (Figure 10) [78]. The strong inorganic-organic interaction between the surfactant and structure layer, proved by 2D $^1$H–$^{29}$Si solid-state NMR, induced the formation of the resultant alternating stacking of inorganic MWW layers and the organic CTAB layers. The calcined ECNU-7 zeolite exhibited a hierarchical pore system and larger external surface area than that of 3D MWW zeolite. Heteroatoms, like Al and Ti, can be isomorphously incorporated into the ECNU-7 zeolite, and they showed a superior catalytic activity in the cracking of 1,3,5-triisopropylbenzene and the epoxidation of propylene with bulky cumene hydroperoxide as oxidant, respectively, compared to the traditional 3D MWW zeolite [79].

Figure 9.
Scheme description of intergrowth ECNU-5 zeolite with novel MWW layer arrangement by rapid dissolution-recrystallization method.
4. Conclusions

Layered zeolites, composed of zeolitic nanosheets linked by hydrogen bonds, provide modifiable precursors for the synthesis of novel zeolite derivatives with open pore system or large external surface area. The newly developed synthesis strategies, including the usage of delicately designed bifunctional amphiphilic SDAs and the top-down selective hydrolysis of 3D germanosilicates, have unexpectedly broken the limitation of conventional hydrothermal synthesis and largely expanded the family of layered zeolites. The successful example of layered MFI zeolite synthesized by bifunctional SDA indicated the potential of design synthesis and encouraged the researchers to explore more novel-layered zeolites. The selective degradation of germanosilicates, transforming the 3D zeolite to 2D lamellar zeolite, is highly related to the orientation distribution of instable bonds in the framework. To explore other zeolite structures besides germanosilicates with such regularity is expected to create new layered precursors.

On the other hand, several improved modification procedures have been proposed to simplify the multistep conventional processes and avoid the harsh treatment conditions. The variation of post-synthesis modifications is potential in providing more derivatives for the layered precursors, showing the infinite possibilities of the modifiable 2D layered zeolites.

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Conflict of interest

The authors declare no conflict of interest.

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