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Rational Approaches toward the Design and Synthesis of Zeolitic Inorganic Open-Framework Materials

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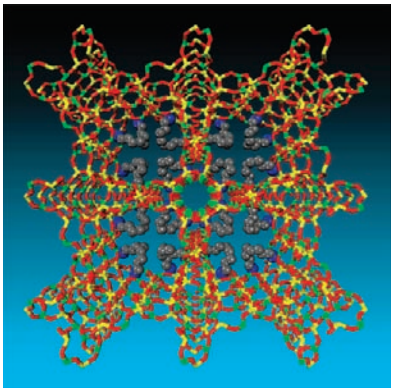

Since the first synthesis of zeolites in 1940s, these materials and related inorganic open-framework materials with regular nanoporous space have attracted considerable interest. Zeolites are important for catalysis, adsorption, and ion-exchange, and researchers are finding new applications for these materials in optics, electronics, sensors, and medicine. In particular, the petrochemical industry is interested in the synthesis of new zeolite catalysts with high catalytic activity and selectivity.

Using hydrothermal, solvothermal, and the recently-developed ionothermal methods, researchers have prepared 194 types of zeolites and thousands of zeolite-related inorganic open-framework materials. However, their syntheses are based primarily on an empirical "trial-and-error" method. The rational synthesis of zeolitic inorganic open-framework materials, while targeting novel structures and functions, remains a formidable task. The challenge in rational synthesis lies in the unknown mechanism for their formation: the relationship between the synthetic parameters and structural characteristics of the products is not clear. In an effort to overcome these challenges, our group has built up a ZEOBANK, a database of zeolite structures and a database for their synthesis. ZEOBANK allows us to use data mining to find new methods for guiding the synthesis of zeolitic materials.

In this Account, we describe our efforts to rationally synthesize zeolitic inorganic open-framework materials with desired structures and present computational methods for the design of these structures. In particular, we focus on the design of zeolites with desired pore geometries through constrained assembly of atoms around the predefined channels in the unit cell. Our approaches toward rational synthesis include the use of template to direct the structure, the use of heteroatoms as a framework substituent, and the use of computational data mining. Employing these strategies, we have developed innovative methods toward the synthesis of target structures with specific channel structures, such as extra-large pores and chiral channels. We expect that further data mining will increase the synthetic control for researchers interested in designing functional zeolitic materials.

1. Introduction

With the ever-growing demands for new zeolite materials with desired structures and functions, the designed synthesis of such materials has aroused considerable attention.[1,2] Zeolites and related inorganic open-framework materials are nanoporous crystalline materials that have widespread applications in catalysis, adsorption, and ion-exchange and are one of the most important catalysts in oil refining, petroleum industry, and fine chemical industry.[3] Their excellent performance is essentially determined by their structural characteristics, such as the size of the pore window, the accessible void space, the dimensionality of the channel system, the numbers and sites of cations, etc. In addition, their properties (e.g., diffusion and catalysis) can be also manipulated through variations in morphology.[4]

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Since the pioneering work by Barrer and Milton in the 1940s, 194 types of zeolites[5] and thousands types of inorganic open-framework materials with unique structures and properties have been discovered.[6] Synthesis of such materials is typically carried out in a gel medium under hydrothermal/solvothermal conditions by using alkali metal ions or organic amines/ammonium cations as the templates or structure-directing agents (SDAs). However, the crystallization kinetics of these materials is very complex, which is dependent on many variables such as the source materials, the gel composition, the pH value, the SDAs, the solvent, the crystallization temperature and time, etc.[7] The difficulty in the rational synthesis of zeolitic materials lies in our limited knowledge of their crystallization mechanism. Nevertheless, the synthesis of new zeolite materials has been greatly advanced during the recent decade through the introduction of new synthetic strategies. Notably, Corma et al. successfully developed a number of new silicogermanate zeolites ITQ-*n* by the use of Ge atoms as a silicon substituent to introduce D4Rs in the structures combined with the design of organic SDA molecules.[8,9] Particularly, computational methods have significantly enhanced researchers' ability in targeting zeolites with specific structures and properties.[10]

Rationalization of the synthesis of zeolitic materials with desirable structures is one of the most fundamental challenges in zeolite science. In this Account, we will illustrate the state of art in this area, mainly highlighting aspects of our research on the rational design and synthesis of zeolitic inorganic open-framework materials. Finally, a future perspective toward the final objective has been described.

2. Computational Design of Zeolite Frameworks

Computational methods in the elucidation of crystal structures and their properties are now well established. Much work has been devoted to the generation of potential new zeolite structures.[11−13] For example, Treacy and co-workers used a symmetry constrained intersite bond searching method to generate over 2 millions of structures.[13] On the other hand, predicting the structures in a rational way is of particular interest with the increasing demand for specific zeolitic materials that fulfill the practical applications. Draznieks, Férey, and coworkers developed the automated assembly of secondary building units (AASBU) method for the prediction of inorganic structures that allows to exploring the possible ways of assembly of predefined inorganic building units.[14] We developed a method for the prediction of open-framework aluminophosphate structures with specific Al/P ratios under the constraints of additional Lowenstein's rule.[15,16]

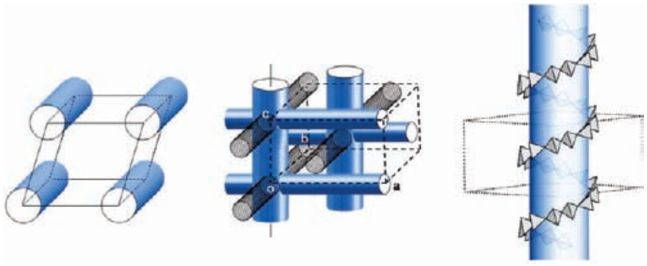

FIGURE 1. Forbidden zones defined as cylinders in one unit cell. Left: 1D channel system. Middle: 3D channel system. Right: Chiral channel system.

A prerequisite for the rational synthesis of zeolitic materials is the capability to design the target porous architectures that are determinant of their performances. In 2003, we developed a computational method for the design of zeolite frameworks with defined pore geometry through constrained assembly of atoms.[17] The central feature of the method is the use of the concept of "forbidden zones" that correspond to the predefined channels.

As illustrated in Figure 1, the channels represented by cylinders are introduced into the unit cell, which define the "forbidden zones" inside which no atoms can be placed during the generation process of a zeolite framework. Such a forbidden zone can be specifically designed to reflect a particular desired porous geometry in the zeolite,[17,18] such as 1D channel, 3D intersecting channel, and chiral channel. Then atoms are assembled out side of the forbidden zones based on symmetry constraint of a specific space group, as well as a distance constraint assuming a Si···Si distance of no less than 3 Å for a typical zeolite structure. Figure 2 shows the generation process for a hypothetical zeolite framework. The idea of this method, that is, constrained assembly of atoms outside of the forbidden zones (channels), is very simple and straightforward, which allows design of zeolites with predefined channel structures under a specific space group. Woodely et al. in 2004 developed a genetic algorithm (GA) method to the design of zeolite structures on the basis of an "exclusion zone".[19]

In 2008, our research group further developed a method to generate zeolite frameworks in density maps.[20] In this method, we integrate the pore information extracted from the density map of HRTEM into the structure modeling. A density map can be built up from one HRTEM image by expanding the 2D image over the unit cell. In this density map, the high density region (black) corresponds to atoms and the low density region (white) to channels. Thus, the 3D density map

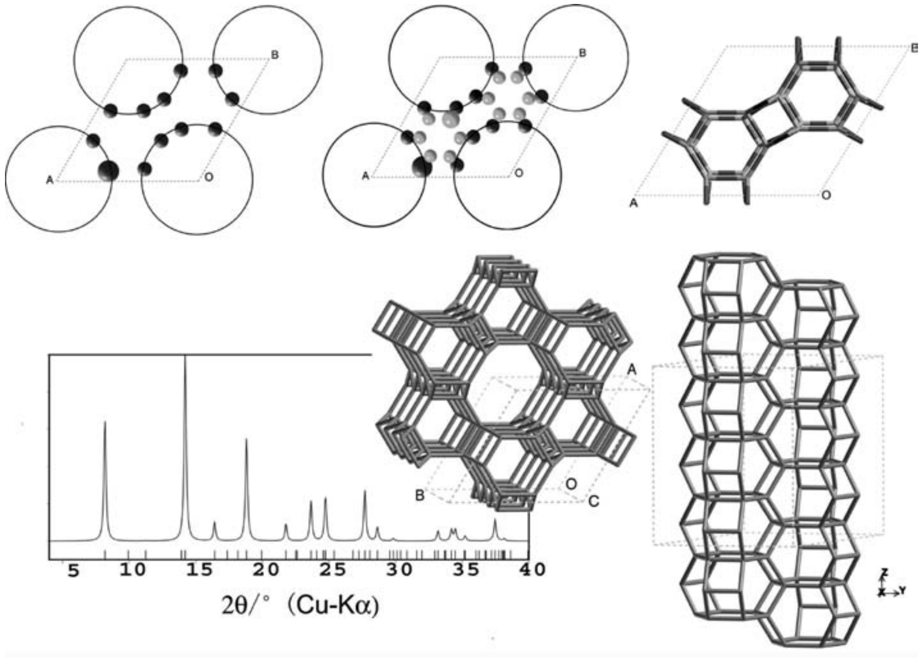

FIGURE 2. Illustration of the generation process for a hypothetical framework H1, assuming the space group of $P6_3/mmc$ ($a = b = c = 15$ Å). The pore radius is set at 6.0 Å. The first unique atom represented by a larger black ball is confined to the pore wall followed by the generation of 23 equivalent atoms using symmetry operation *l* (top left). The second unique atom represented as a larger grey ball is randomly placed outside of the forbidden zones, followed by the generation of 11 equivalent atoms by symmetry operation *j* (top middle). Bridging atoms are added (top right). Framework structure containing 12-ring channels enclosed by columns of can cages along the c axis and the simulated XRD pattern (bottom).

defines the regions (channels) where atoms may not be located. The defined cost terms include bonding, connectivity, and a new term, E_{map} that reflects the degree of agreement between the positions of the T atoms and the density map derived from the HRTEM image. Figure 3 illustrates the generation of the zeolite IM-5 framework in a 3D density map derived from one HRTEM image. By using this method, it is able to solve the most complex zeolite structures. Furthermore, this method can be applied to the prediction of new structures with desired pore structures. We can define a density map reflecting the desired porous pattern and then generate structures with such pore geometry.

Our group has built up a hypothetical zeolite database that contains the not-yet-discovered zeolite structures which were predicted.[21] One can easily search the structures by inputting the defined structural characters, such as the pore system, pore size, SBU, etc. Further access of these novel structures will be achieved with the aid of rational template design, as well as innovative synthetic strategies.

3. Chemical and Physical Problems on Way to the Rational Synthesis of Zeolitic Materials

Computational simulation has proven to be a powerful tool for designing interesting but not yet discovered zeolite structures. However, how to access the target zeolite structures synthetically is one of the most formidable issues in zeolite and materials science. Although zeolite synthesis has been extensively studied during the last six decades, the rational synthesis is still far behind the empirical trial-and-error synthesis. This identifies the challenges and problems that remain in this area. Zeolite crystallization represents one of the most complex chemical problems in crystallization phenomena, such as polymerization−depolymerization, solution−gelation, and nucleation-crystallization. It involves complex reactions and quasi-equilibria between solid and solution components during the crystallization process. Elucidating the formation pathway has been one of the major challenges in zeolite science.[22] Until now, however, there is no sufficient understanding of the formation mechanism of zeolites by which amorphous gels are converted to the porous crystalline solids at the molecular level. Especially, there is no understanding on how to control the self-assembly of reaction species that determines the formation of a specific zeolite structure under a given set of synthesis conditions. This significantly limits the synthesis of zeolites in a predictable way.

A typical crystallization procedure of zeolitic materials involves the use of inorganic cations or organic templates, also called structure-directing agents (SDAs) under hydrothermal or solvo-

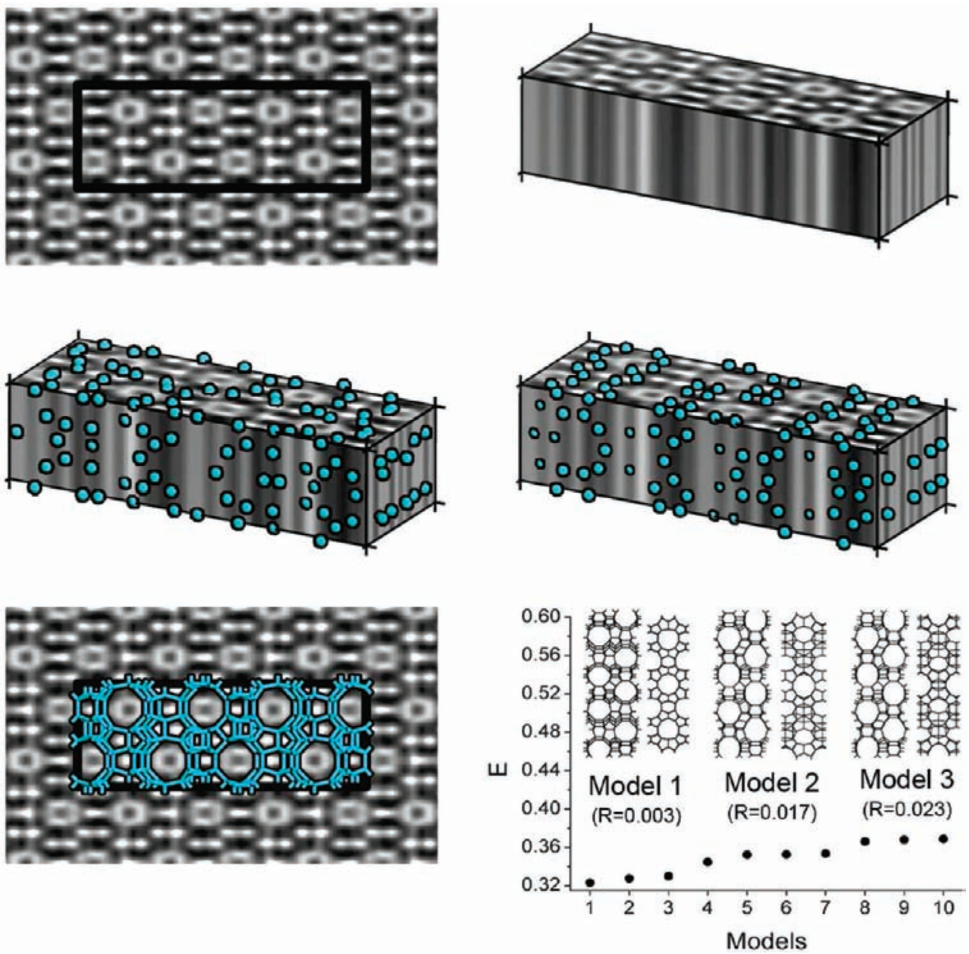

FIGURE 3. Generation of the IM-5 framework in a three-dimensional density map derived from one HRTEM image along the [100] direction. Top left: The HRTEM image of IM-5 along the [100] direction. Top right: The density map generated from the image shown in top left. Middle left: T atoms placed randomly in the density map at the beginning of the simulation. Middle right: T atoms rearranged in the density map during the simulation. Bottom left: Agreement between the generated structure model and HRTEM image along the [100] direction. Bottom right: Plot of the cost values of the generated structure models. All generated models are unique, and only the ten models with the lowest cost values are shown. Model 1 has the lowest cost value and the best R_{DLS} value, and it corresponds to the correct structure solution. Its framework projections along the [100] and [001] directions are displayed together with those of two other models with low cost values.

thermal conditions. The self-assembly of the crystalline open-framework structures with the SDA molecules is an extremely complex chemical process, involving changes over the small (primary units), to medium (nuclei), to large scale (crystallites).[23] Unlike the organic synthesis, there are no defined reactions in such complex inorganic—inorganic and organic—inorganic system mediated by the water or nonaqueous (e.g., alcohol, ionic liquid) solvent. Moreover, currently there is a lack of advanced characterization techniques that can detect the reaction species during the crystallization process. So far, a variety of analytical techniques, such as advanced nuclear magnetic resonance (NMR) spectroscopy, high-resolution electron microscopy (HRTEM), atomic force microscopy (AFM), small-angle X-ray and neutron scattering (SAXS and SANS), electrospray ionization mass spectrometry (ESI-MS), UV-Raman, etc., as well as combinations of them with computer simulations, have been used to study the formation of zeolitic materials. However, none of these techniques could provide a clear picture of detailed chemical steps occurring during the crystallization of a zeolite. Time-resolved in situ experimentation following the changes that occur with time at the molecular level represents a significant physical problem in zeolite science as well. To finely control the chemical steps toward the formation of a given zeolitic open framework is far beyond our current capabilities. A better understanding of the formation mechanism is essential for a rational zeolite design.

4. Attempts toward the Rational Synthesis of Zeolitic Inorganic Open-Framework Materials

In the proceeding section, we have addressed the chemical and physical problems faced on way to the rational synthesis of zeolitic materials. Despite that, many research efforts have been made toward the synthesize of tailor-made zeolitic materials with target structures. Some rational approaches have been developed in light of knowledge gained from the extensive trial-and-error synthesis, as well as the understanding of the key effect of some synthetic factors on zeolite formation. Especially, computational methods have greatly assisted in targeting zeolites with specific structures and properties. Our group has developed a new way to guide the synthesis of zeolitic materials through data-mining of the complex relationship between the synthetic factors and structural features.[24,25] In this section, we will present the current attempts to the rational synthesis of zeolitic inorganic open-framework materials. By means of the new synthetic approaches, zeolitic materials with specific structures are accessible in a more rational way.

4.1. Synthesis Guided by the Structure-Directing Effect of SDAs. Zeolite synthesis is typically driven by templates or SDAs.[26] However, the specific role of SDAs in complex assembly to highly ordered open frameworks remains unclear at the molecular level. Although a direct analogy between the SDA and the resultant channel space cannot be clearly established, there is ample evidence that the SDA does have an influence on defining the channel geometry.[27] Specifically, computer modeling has proven to be useful for examining the structure directing effects of known molecules, as well as predicting suitable SDAs for a given structure in terms of the host−guest interaction.[28,29]

Lewis et al. developed a method for de novo design of SDA molecules, which can be computationally "grown" within the confines of the pore system for a specific microporous structure.[30] This method demonstrates its potential in developing new SDAs for different known types of zeolite topologies, and also for new zeolitic materials with desired framework structures.

We developed a computational method for the prediction of the templating ability of organic amines in the formation of open-framework aluminophosphates.[31,32] These compounds show diverse structural architectures with 1D chain, 2D layer and 3D open-framework structures.[33] Their open-framework structures are greatly manipulated by organic SDA molecules that interact with the host framework through nonbonding interactions. In terms of the energies of the host−template nonbonding interactions, the templating ability of various organic amines for the inorganic hosts can be predicted. Some suitable SDA candidates can be selected that have lower interaction energies with a given host. One of the successful examples is the syntheses of $Al_4P_5O_{19}(OH)\cdot C_5N_2H_{16}$ (AlPO-PDA) and $Al_4P_5O_{19}(OH)\cdot C_4N_3H_{15}$ (AlPO-DET) with structures analogous to that of AlPO-HDA by rational selection of 1,5-pentanediamine and diethylenetriamine as templates that are predicted by molecular simulations.[32]

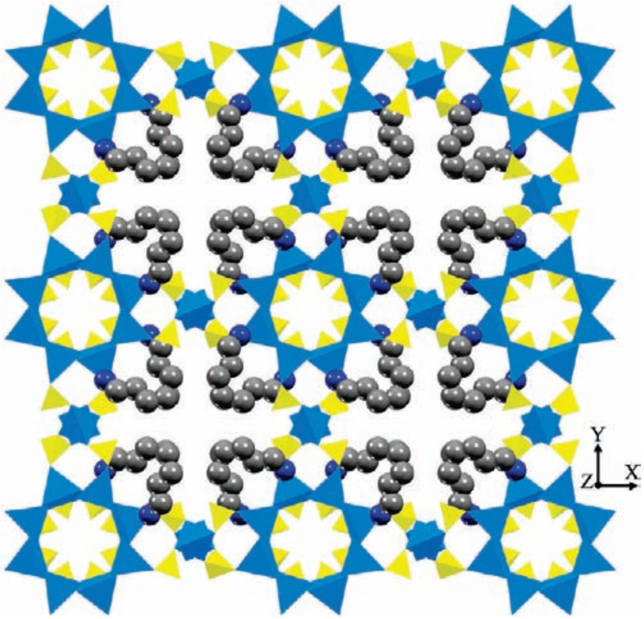

FIGURE 4. Open-framework structure of ZnHPO-CJ1 viewed along the [001] direction. Each 24-ring channel accommodates multiple small protonated *n*-butylammonium cations.

By utilizing organic amines that are predicted by computer simulations as the SDAs, such as cyclohexylamine (CHA), cyclopentylamine (CPA), and *n*-propylamine, three open-framework zinc phosphites, including $(C_6H_{14}N)_2[Zn_3(HPO_3)_4]$ (ZnHPO-CJ2), $(C_5H_{12}N)_2[Zn_3(HPO_3)_4]$ (ZnHPO-CJ3), and $(C_3H_{10}N)_2[Zn_3(HPO_3)_4]$ (ZnHPO-CJ4), have been hydrothermally prepared with target extra-large 24-ring channels analogous to $(C_4NH_{12})_2[Zn_3(HPO_3)_4]$ (ZnHPO-CJ1).[34,35] The synthesis of ZnHPO-CJ1 demonstrates the cooperative templating mechanism of multiple small organic cations in the formation of extra-large-pore open-framework structures with high framework charge density. As seen in Figure 4, each 24-ring channel of ZnHPO-CJ1 accommodates multiple small protonated *n*-butylammonium cations. Notably, the hydrophobic ends of the SDA molecules point toward the void space, while the hydrophilic ends point toward the pore wall, which resembles the supramolecular micellar arrangements in the synthesis of mesoporous materials. This mode of structure direction permits the use of the cooperative effect of multiple small organic SDAs in the synthesis of zeolitic materials with extra-large pores. Our studies on the host−guest relationship in some known extra-large-pore open-framework compounds demonstrated that the templating ability of the organic amines can be evaluated in terms of the charge-density matching, space matching, and nonbonding interactions of the host framework and the guest SDA molecules.[36]

The combinatorial approach or high-throughput technique allows exploration of the synthesis in a large experimental space by means of appropriate experimental design, which has been used in the hydrothermal/solvothermal synthesis of zeolitic inorganic open-framework materials in recent decade.[37,38] We further demonstrated a powerful strategy toward the rational synthesis of zeolitic materials by combination of computational and combinatorial approach, taking aluminophosphate molecular sieve AlPO_4-21 as an illustration.[39] In terms of nonbonding interaction energies of host−guest calculated by molecular simulations, the templating abilities of various organic amines in the formation of AlPO_4-21 have been evaluated. Through rational selection of the predicted suitable templates, such as ethanolamine, ethylamine, dimethylamine, and *n*-propylamine, etc., AlPO_4-21 has been successfully synthesized by hydrothermal combinatorial approach in the reaction system with molar composition $1.0\text{Al}(^{i}\text{OPr})_3/x\text{H}_3\text{PO}_4/y\text{R}/255.0\text{H}_2\text{O}$ (R = amines) at 180 °C for 5 days.

4.2. Synthesis Guided by Substituent Element Effects. In recent years, the use of germanium as a silica substituent combined with the use of novel SDAs by Corma et al. has led to the discovery of a number of novel silicogermanate zeolites.[8,9] The rationale behinds this discovery is to apply the concept of isomorphous substitution for directing D4R-containing zeolites.[2] The structure-directing effect of Ge toward the formation of D4R-containing zeolites is because the smaller Ge−O−Ge angles as compared to the Si−O−Si angles, can relax the geometric constraints in the D4R units and thus stabilize the resulting structures. A remarkable example is synthesis of mesoporous chiral zeolite ITQ-37 that is achieved by combining a synthesis guided by substituent element effect and high throughput technique.[40]

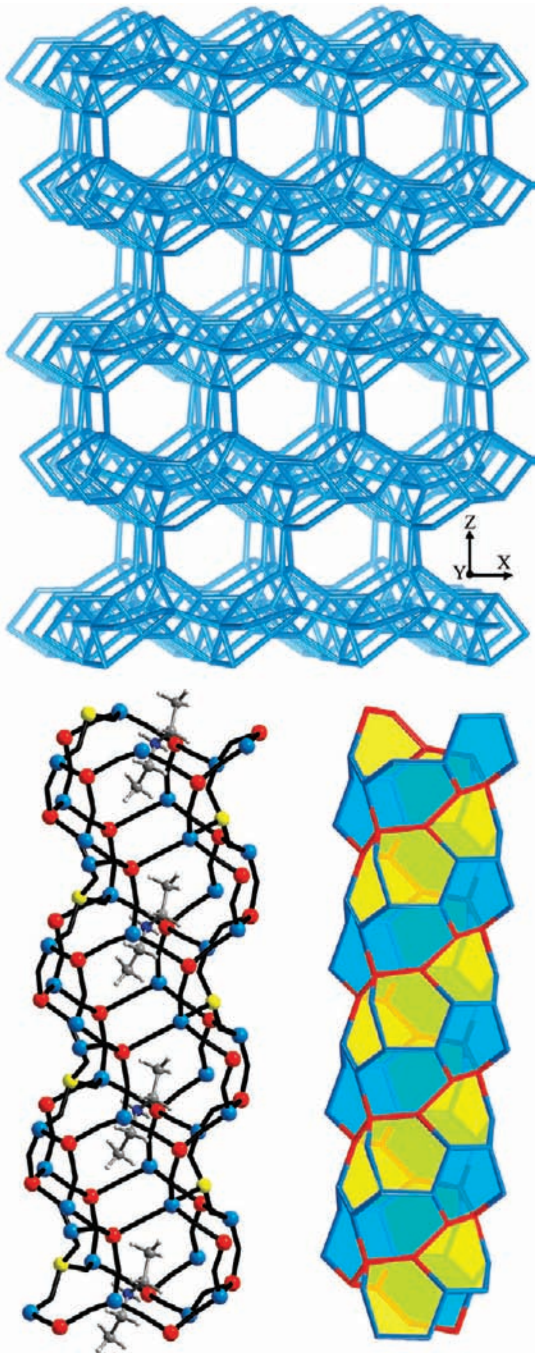

FIGURE 5. Framework structure of CoAPO-CJ40. Top: Viewed along the [010] direction. Bottom left: The helical 10-ring channel and helical arrangement of cobalt atoms (yellow color for Co). Bottom right: The 10-ring channel enclosed by double helical ribbons made of the edge-sharing of six-rings.

Heteroatoms have also demonstrated their effect on stabilization of the chiral zeolite frameworks as observed by our recent work. We have developed a method for the design of chiral zeolite frameworks with specified pore geometries through constrained assembly of atoms.[18] According to the calculation results, most four-connected frameworks generated with chiral channels are energetically unfavorable for the SiO_2 composition because of the special geometric strains in such structures. This suggests that introducing other elements, such as Be, B, Ge, and transition metals, instead of Si, might be a promising strategy for stabilizing such frameworks because they could offer a more reasonable bonding geometry, such as bond distances and bond angles, than an SiO_2 composition does. By the incorporation of metal ions (Co^{2+}, Mg^{2+}, Fe^{2+}, etc.) into the aluminophosphate framework, we have for the first time solvothermally synthesized novel heteroatom-containing chiral aluminophosphate MAPO-CJ40 (M = Co^{2+}, Mg^{2+}, Fe^{2+}, etc.) with one-dimensional helical 10-ring channels.[41] Figure 5 shows the structure of CoAPO-CJ40. The structure is based on the strict alternation of MO_4 (M = Al, Co) and PO_4 tetrahedra forming an anionic $[Co_2Al_{10}P_{12}O_{48}]^{2-}$ framework. Charge neutrality is achieved by protonated diethylamine cations. The helical 10-ring channels are enclosed by double helical ribbons of the same handedness made of the edge-sharing of six-rings along the 2_1 screw axis. The Co atoms, which substitute one of the three unique Al sites, adopt a helical arrangement along the channel. The framework of CoAPO-CJ40 is intrinsically chiral and exhibits a new zeotype structure assigned as JRY.[5] Molecular simulations and geometric calculations demonstrated that Co^{2+} ions play an important role in stabilizing the chiral framework. The successful synthesis of MAPO-CJ40 provides an insight toward targeting chiral heteroatom-containing aluminophosphate molecular sieves as potential single-site chiral solid catalysts.

4.3. Synthesis Guided by Data Mining. Taking account of the chemical and physical problems on way to the rational synthesis of zeolitic inorganic open-framework materials, we have been attempting to explore another route to guide the synthesis of zeolitic materials through data mining. Since open-framework aluminophosphates (AlPOs) constitute an important family of zeolites and related microporous materials and show rich structure chemistry,[42] we take AlPOs as an example to explore the basic mode for the designed synthesis of zeolitic materials through data mining. To achieve this, our research group has established a multidatabase Zeobank,[43] consisting of a database of AlPO synthesis,[44] a database of AlPO structures,[45] and a database of hypothetical zeolite structures.[21] The Zeobank will allow us to apply computational techniques to study complex relationships between the synthetic parameters and the corresponding zeolite structures in a systematic manner. Statistical relationships between experimental conditions and the products can be established by utilizing classification techniques,[46] such as support vector machines (SVMs) and neural network.

We recently reported a SVM-based computational study for predicting the formation of (6,12)-ring-containing microporous AlPOs.[25] Through analyses of a database of AlPO synthesis with ~1600 reaction data, we identified a number of synthetic parameters, such as three gel molar ratios of Al_2O_3 (F1), P_2O_5 (F2), and the organic amine template (F4), as well as a number of parameters associated with the geometric and electronic characteristics of the templates as the input. Eleven template parameters which are believed to cover most important features of a template are considered, including the longest distance (F11), the second longest distance (F12) and the shortest distance (F13) associated with the template geometry, the van der Waals (VDW) volume (F14), the dipole moment (F15), the ratio of C/N (F16), the ratio of N/(C+N) (F17), and the ratio of N/VDW volume (F18) in the template, the Sanderson electronegativity (F19), the number of freely rotated single bond (F20), and the max H^+ number (F21). Using these parameters, we have trained a SVM-based classifier on a training data set containing 363 (6,12)-ring containing AlPOs and 1069 AlPOs without such rings. In our work, three important features related to the molar ratios of Al_2O_3, P_2O_5, and the organic template in the starting gel and the 11 template parameters are used as the input parameters for training the classifier. The output of the trained classifier is either 0 or 1, if a resulting structure contains a (6, 12)-ring or not.

We have tested each synthetic parameter individually and some in combination and checked which ones may have the predictive power in distinguishing the two classes of AlPOs. For example, we found that a classifier using only three synthetic parameters involving the molar ratios of Al_2O_3 (F1), P_2O_5 (F2), and template (F4) cannot predict if an AlPO contains (6,12)-rings or not. Further introducing the 11 aforementioned template parameters, along with the three synthetic parameters, individually or grouping combinations, as the classification inputs leads to substantially different levels of classification performance. This reveals that the choice of suitable template parameters is of vital importance in the classification performance.

By analyzing the classification performances using different combinations of the template parameters with Al_2O_3 (F1), P_2O_5 (F2), and template (F4), we have identified the most relevant template parameters to our classification problem. Notably, we found that the second longest distance within each template (F12) has the best prediction performance among all individual parameters, giving a training accuracy of 80.54% and a testing accuracy of 78.08% by itself. Further combination of F12 with another electronic parameter of the template, such as F16 (the ratio of C/N) or F18 (the ratio of N/VDW volume), gives the training accuracy 83.66%−84.31% and the testing accuracy 81.61%−81.75% (Table 1).

Our studies demonstrate the general feasibility in establishing a relationship between the synthetic parameters and the structural characters of the synthesized zeolitic materials, thus providing a useful guidance to the rational synthesis of such materials as well as other inorganic crystalline materials. It is believed that with more reaction information as the input, for example, chemical components (precursor species, nuclei, etc.) in the reaction system, it might be possible to establish the reaction pathways within the "black box" sys-

TABLE 1. Sets of Input Template Parameters Exhibiting Highest Accuracy

N[a]	template parameters											training accuracy (%)	testing accuracy (%)
1	F12											80.54	78.08
2	F12	F16										84.31	81.75
3	F12	F16	F21									85.74	82.06
4	F12	F15	F16	F17								86.94	82.31
5	F12	F15	F16	F17	F18							87.51	82.44
6	F12	F13	F14	F15	F18	F19						87.86	82.36
7	F12	F13	F14	F15	F17	F19	F21					87.94	82.36
8	F12	F13	F14	F15	F17	F18	F19	F21				87.97	82.17
9	F12	F13	F14	F15	F16	F17	F18	F19	F21			87.97	82.08
10	F12	F13	F14	F15	F16	F17	F18	F19	F20	F21		87.99	81.97
11	F11	F12	F13	F14	F15	F16	F17	F18	F19	F20	F21	87.98	81.64

[a] *N* is the number of input template parameters.

tem in zeolite formation, thus opening a new way to gain some insight into the formation mechanism of zeolitic materials.

Currently, various computation techniques have been used to retrieve knowledge from the data analysis,[47] such as neural networks, support vector machines, classification trees, clustering analysis, principal component analysis, control theory, etc. For example, Baumes et al. showed how data mining techniques offer a solution for detecting a potential new structure from a synthesis that produces a mixture of zeolitic structures.[48] Even though computational data mining techniques show a great promise in guiding the rational synthesis of zeolitic materials, it has to be stressed that the successful prediction of the formation of these materials with specified structural features will heavily rely on our deep understanding of zeolite synthesis chemistry.

5. Future Perspective on the Tailor-Made Synthesis of Desired Zeolitic Materials

Zeolitic materials are of immense importance in many technological processes, such as catalysis, adsorption, and separation because of their unique pore topologies and the possibility to introduce active reaction sites. Especially, zeolites are very successful catalysts in shape-selective catalysis that have found many industrial applications. Fine tuning zeolites with controlled pore architectures, such as the pore system, pore size, and pore shape, will improve their performance for applications. Clearly, this represents a formidable challenge and will call for a capability to tailor-made synthesis of zeolitic materials with desired structures and functionalities.

Currently, computational approaches combined with extensive experimental work, as well as accumulated knowledge of property-structure-synthesis, have greatly assisted in rationalizing the synthesis of zeolitic materials. Figure 6 depicts the future blueprint for the tailor-made synthesis of desired zeolitic materials. The engineering to access the target functional zeolitic materials can be described as the following: (i) A practical application, for example, a specific catalytic reaction, raises particular requirements for the zeolite structures with defined pore dimension, pore size, pore shape, active sites, etc. (ii) The desired zeolite structures are then designed by computational methods. (iii) The candidate SDA molecules are predicted for the given structures by using computational modeling. Further data mining techniques will predict the synthesis conditions for the target structures. (iv) The synthesis is accessed by using various synthetic techniques under hydro-

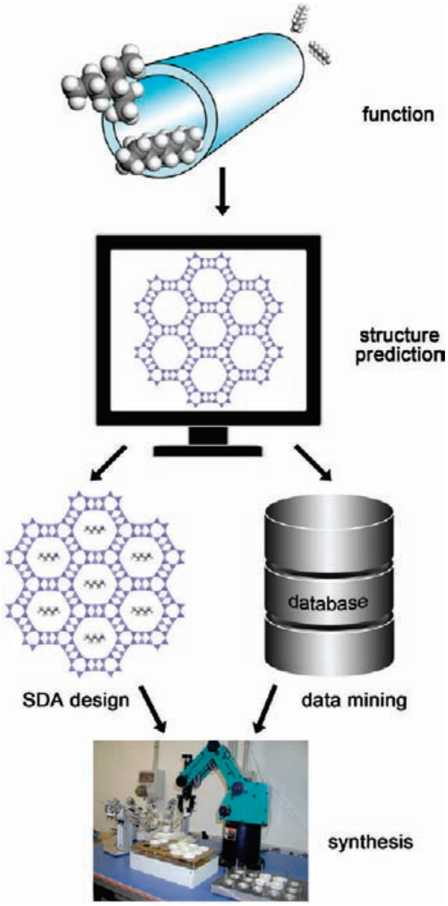

FIGURE 6. Future blueprint for engineering the rational synthesis of zeolitic materials with desired functionalities and structures.

thermal or solvothermal conditions. Combinatorial techniques, especially, will allow the exploration in a large experimental space by means of the appropriate experimental design. (v) The structures of the as-made materials are identified by comparing the experimental X-ray diffraction patterns with the simulated ones derived from the theoretical structures. (vi) The application is eventually accessible by such a rational design and synthesis approach.

It is worth noting that there are a number of challenges ahead in the path toward the rational zeolite synthesis. Although great strides have been made in this area, future advances in understanding the formation mechanism of zeolitic materials at the molecular level are essential before the promise is fulfilled. Our dream is to chemically control the self-assembly process of zeolitic porous materials with predictable structures and functionalities, and eventually to replace the empirical trial-and-error strategy by the *ab initio* design. This is, in fact, a long journey from possibility to reality. Yet despite the difficulties, this is the way the zeolite chemists should go. More research, as well as long-term efforts, should be driven along these directions. We hope this Account will stimulate the advance of this exciting and challenging research area in zeolite science.

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BIOGRAPHICAL INFORMATION

Jihong Yu obtained BS (1989), MS (1992), and PhD (1995) degrees from Jilin University and worked as a postdoctral fellow first at the Hong Kong University of Science and Technology and then at Tohoku University, Japan, during 1996−1998. Since 1999, she has been a full Professor in the Chemistry Department, Jilin University, has been appointed as the Cheung Kong Professor since 2007. Her research interest is the design and synthesis of zeolite and related inorganic open-framework materials.

Ruren Xu obtained a BS degree from the National Shanghai Jiaotong University (1952) and worked at Fudan University and Hamburg University. Since 1979, he has been a Professor in the Chemistry Department, Jilin University. His research interest is in molecular engineering of zeolite and porous materials. He is an academician of the Chinese Academy of Sciences (since 1991) and the Fellow of the Third World Academy of Sciences (since 2003).

FOOTNOTES

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