



## Zeolite Crystal Engineering

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## **Zeolite Crystal Engineering**

Zeolites have been the most important industrial adsorbents and catalysts in the energy and petrochemicals sector and grow rapidly in innovative applications in new energies and advanced functional materials. However, while the production of zeolites has undeniably reached an industrial maturity, and despite considerable research efforts focused on these materials during the last few decades, understanding the mechanisms governing their synthesis remains a major and tough challenge. Consequently, the fine control of their properties and the discovery of new materials often rely on empirical trial-and-error screening rather than through fundamental scientific directions, which poses a bottleneck for fast development of new materials and next-generation products.

This virtual special issue (VSI) in Crystal Growth & Design showcases the latest developments in the design, synthesis, characterization, and applications of zeolites and other porous materials from leading researchers in this field and includes papers devoted to one or more of the following topics: (i) zeolite formation mechanisms, (ii) designs for state-of-the-art materials (e.g., nanosized or hierarchical materials with unique functionality), (iii) structure–property–performance relationships for novel materials, (iv) new structures and/or established relationships between synthesis conditions and physicochemical properties, (v) zeolite size and morphology control, and (vi) postsynthetic methods of zeolite design. As editors and guest editors, we have taken the liberty to group the contributions to this VSI into the following themes that are significant to current and future directions in the field of zeolite crystal engineering.

## **Understanding Fundamental Processes of Porous Materials Crystallization**

The need for zeolites with optimal properties for a range of applications calls for an improved fundamental understanding of the factors involved in materials synthesis. The number of variables in zeolite synthesis is a daunting task for experimental design. Many studies have examined the role of key reagents, including the selection of silica/alumina sources, inorganic/organic structure-directing agent cations, and corresponding anions.<sup>1–3</sup> Seed-assisted syntheses are being more commonly recognized as versatile approaches in zeolite crystal engineering. For instance, interzeolite transformation (IZT) from an initial (parent) to a final (daughter) crystal<sup>4,5</sup> can often produce materials with properties that cannot be achieved by conventional methods. There has been increased efforts to understand mechanisms of crystallization for known zeolites, design synthesis methods to achieve new structures,<sup>6</sup> and establish databases of hypothetical structures to guide future synthetic efforts.<sup>7</sup> Elucidating processes of nucleation and

growth rely on the characterization of growth species, which range from dissolved (alumino)silicates with diverse speciation to amorphous precursors that evolve during synthesis.<sup>8,9</sup> The nature of the sol–gel medium, including the relative contributions of solution and solid phases, can markedly impact the kinetics of crystallization, as well as the physicochemical properties (e.g., crystal size, morphology) of the zeolite products.

## **Controlling Aluminum Composition and Siting**

It has been known for some time, but is becoming increasingly more evident, that the ability to control the number and spatial arrangement of aluminum in zeolite frameworks can have a profound impact on materials properties and their performance in applications, particularly in the area of catalysis. Aluminum siting can be controlled by the judicious selection of one or more structure-directing agents or by the use of seeds or IZT synthesis methods.<sup>10–12</sup> Control of aluminum composition can impact physical properties, such as unit cell volume<sup>13</sup> or hydrothermal stability,<sup>14</sup> which can impact their performance in applications spanning separation to catalysis.

## **Moving Beyond Aluminum: Introduction of Heteroatoms**

In zeolite catalysis, many reactions require the introduction of different metals, either as framework or extra-framework species, to tune the Lewis and/or Brønsted acidity of the zeolitic materials. There has been a substantial increase in the number of studies focused on synthesizing and testing Ti-zeolite

catalysts. 15 The most commonly studied is TS-1 (MFI-type zeolite). 16 However, there are also efforts to introduce titanium in other frameworks (e.g., MSE-type zeolite). 17 Moreover, synthesis of zeolites with other metals (e.g., Fe, Ga, etc.) is described in this virtual special issue.<sup>18,19</sup>

### **Nanosized and Hierarchical Zeolites**

Mass transport limitations in zeolites have motivated efforts to design materials with nanosized or hierarchical (e.g., mesoporous, pillared, etc.) architectures.<sup>20–22</sup> Soft templating techniques have been used as bottom-up approaches,<sup>23</sup> whereas postsynthesis modification offers a top-down approach<sup>24</sup> to enhance diffusion properties of zeolitic materials. Methods that combine heteroatom (e.g., Ti) incorporation in the design of hierarchical materials is also discussed in this virtual special issue.<sup>25,26</sup>

### **Elucidating and Optimizing Structure-Performance Relationships**

Advancements in the understanding of crystallization pathways and the design of new synthetic methods are often coupled with developing an improved understanding of structure–performance relationships for diverse energy applications. This includes the effects of zeolite crystal size,<sup>27</sup> Al siting,<sup>28</sup> heteroatom incorporation,<sup>29,30</sup> and hierarchical architectures.<sup>31</sup>

### **New Approaches in Porous Materials Synthesis and Characterization**

This virtual special issue also includes nonconventional methods of synthesizing nonzeolitic porous materials, such as metal–organic frameworks (MOFs)<sup>32</sup> and mixed metal oxides.<sup>33</sup> Synthesis methods employing low quantities of solvent have shown promise for preparing materials with unique properties,<sup>34</sup> whereas staged syntheses, when either a reagent or reaction condition is altered midsynthesis, can offer a unique route to control processes of crystallization.<sup>35</sup> In this virtual special issue, there are also studies focusing on new methods of characterization, both ex-situ and in situ, to improve our understanding of crystallization processes and offer better diagnostic tools.<sup>36</sup>

This virtual special issue is dedicated to Prof. Svetlana Minotova in honor of her 60th birthday. Prof. Mintova is an internationally renowned scientist in the field of porous materials research, with a focus on zeolite crystallization. As the current Research Director at the French CNRS, she played an integral role in transforming the Laboratory of Catalysis and Spectrochemistry (LCS) at ENSICAEN into a world-class facility for porous materials research. Her impact is evident by the more than 350 publications, 20 patents, numerous awards and invited talks, and her service to the porous materials community as current President of the International Zeolite Association (IZA) and the Federation of European Zeolite Associations (FEZA). This issue is meant to highlight the tremendous progress that has been made in the area of zeolite crystal engineering. We look forward to continuing to feature the community's progress in addressing these stimulating challenges and opportunities in the years to come.

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### **■ AUTHOR INFORMATION**

#### **Notes**

Views expressed in this editorial are those of the authors and not necessarily the views of the ACS.

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