

# Stable 3D extra-large pore zeolites, challenge and opportunity

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As a crucial catalyst material in the chemical industry, the synthesis of new types of zeolites, particularly stable three-dimensional (3D) extra-large pore zeolites with pore openings exceeding 12-membered rings (12-MR), has posed a formidable challenge in zeolite science. In this perspective, we unveil innovative design concepts for structure-directing agents (SDAs) and elucidate the discovery of a transformative 1D to 3D topological condensation mechanism. These breakthroughs propel the creation of stable 3D extra-large pore zeolites from an idea to a reality. Furthermore, the emerging opportunities for their synthesis and potential applications are also envisaged.

## INTRODUCTION

Zeolites are renowned for their high specific surface area, ordered pore structure, tunable active centers, and outstanding hydrothermal stability. These properties make them indispensable as catalysts and adsorbents in traditional chemical industries and well-suited for use in emerging applications such as environmental protection, healthcare, and beyond.<sup>1</sup> Currently, only about 20 types of zeolites have been industrially applied, all featuring pore systems with no more than 12-membered rings (MR). To address the practical demands of applications like heavy oil conversion and macromolecular catalysis, there is an urgent need in the industry for the development of new stable three-dimensional (3D) extra-large pore zeolites. Over the past thirty years, more than twenty types of extra-large pore zeolites have been synthesized. Unfortunately, their practical applications have been hindered by some factors. Firstly, most of these materials require the introduction of germanium in the synthesis, which increases their cost and significantly reduces their thermal and hydrothermal stability. Secondly, many of these materials are "interrupted frameworks" rather than true zeolites, lacking stability at high temperatures and suffering from reduced pore sizes due to terminal groups. Only a few structurally stable and fully connected extra-large pore zeolites exist as pure silicon or aluminosilicate. However, these are only limited to 1D pore systems, such as VPI-5, SSZ-59, SSZ-53, UTD-1, and CIT-5, posing significant mass transfer limitations. The creation of stable 3D extra-large pore zeolites holds substantial theoretical and practical significance and has been a sought-after goal in inorganic synthesis. Recently, we reported the ZEO series of stable 3D extra-large pore zeolites, marking a significant breakthrough in this field from scratch.<sup>2-4</sup>

## INNOVATIVE DESIGN CONCEPTS FOR STRUCTURE-DIRECTING AGENTS

Zeolites are known for their unique porous structures, which are typically thermodynamically unfavorable to form. SDAs, in this process, play a critical and often decisive role by guiding the structure formation and filling the

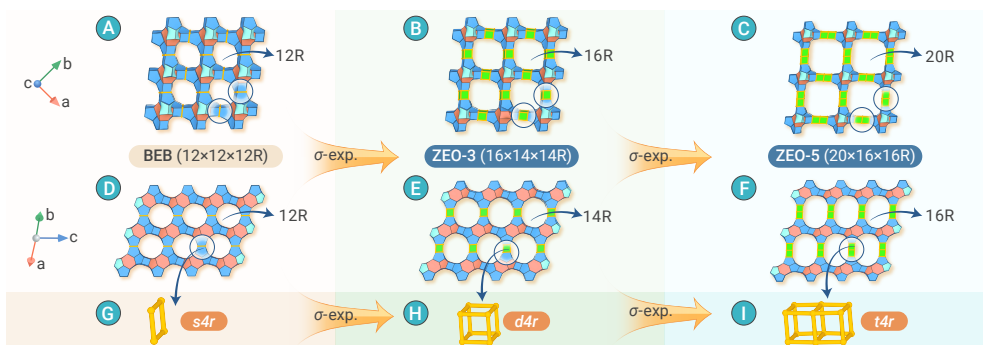
pores. In recent years, we have developed innovative design concepts for SDAs, including the supramolecular assembly templating (SAT) approach and a configuration adaptation method.<sup>2,3,5-8</sup>

The central premise of the SAT approach is that SDAs with small molecular sizes typically struggle to direct the formation of large and extra-large pore zeolites. However, if strong molecular interactions exist between the SDAs, they can self-assemble into larger structures. These larger assemblies then act as effective directing agents, thereby facilitating the efficient formation of large and extra-large pore zeolites.

Through the SAT approach, a series of easily prepared, small, and simple aromatic-containing semi-rigid imidazolium SDAs were designed and synthesized. By using these SDAs, several germanosilicate zeolites with large and extra-large pore were successfully obtained, including ITQ-37 and ITQ-43, which were previously challenging to synthesize with regular SDAs.<sup>9</sup> This approach was found to be an effective and universal method for the synthesis of large and extra-large pore zeolites, and some new types of zeolites named the NUD series were also successfully unearthed.<sup>5-8</sup> NUD-1 with interconnecting 18-, 12-, and 10-MR channels, is the first example of a new framework synthesized using the SAT approach. Its structure is closely related to those of ITQ-33 and ITQ-44, with all three zeolites built from different stackings of the same building layer. NUD-1 consists of single 3-MR, double three-ring silica units (*d3r*), and *d4r* units, which have not been observed in any other known zeolites.<sup>7</sup> Two additional germanosilicates, NUD-2 and NUD-3 were also synthesized under similar conditions.<sup>8,10</sup> NUD-2 is an extra-large pore zeolite with a 2D interconnecting 14MR and 10MR channel system, while NUD-3 possesses a 3D system of large pore channels that is topologically close to those of ITQ-21 and PKU-14.

This concept was further extended to pure silica and aluminosilicate systems using benzimidazolium as SDAs. NUD-5 and NUD-6 were successfully synthesized.<sup>5,6</sup> NUD-5 has a zeolite framework with 1D 14-membered ring pore channels, isostructural to that of UTD-1, which previously required cobaltocene complexes as SDAs. Unlike UTD-1, where SDAs could not be completely removed by calcination due to the presence of cobalt, the inexpensive SDAs in NUD-5 can be fully removed by calcination, and aluminum can be directly incorporated into the NUD-5 framework during synthesis, demonstrating advantages over UTD-1. Furthermore, the aggregation state of SDAs in NUD-5 and NUD-6 differs significantly. In NUD-5, SDAs form 1D supramolecular assembly chains based on  $\pi$ - $\pi$  and CH- $\pi$  interactions, whereas in NUD-6, SDAs are present as individual supramolecular dimers. These results further confirm that the SAT approach is a general and applicable strategy for the synthesis of large and extra-large pore zeolites.

The SAT approach is confirmed to be highly efficient, however, there are still some disadvantages. First, it is difficult to achieve accurate and



**Figure 1. Generation of extra-large pores by 1D to 3D topological condensation** A  $\sigma$ -expansion ( $\sigma$ -exp.) of (A,D) polymorph B of the 3D large-pore zeolite Beta (here denoted as BEB) converts an (G) *s4r* into (H) *d4r* and generates (B,E) the 3D extra-large-pore ZEO-3, whereas a  $\sigma$ -exp. of ZEO-3 converts a *d4r* into a (I) *t4r* and generates (C,F) ZEO-5, with even larger pores.

quantitative control of the SDAs' aggregate state, making the synthesis arbitrary and reliant on trial and error. Second, most of the as-synthesized zeolites have only 1D extra-large pores, likely due to the adverse effects of supramolecular interactions between the SDAs, which primarily contribute to the "filling effects." Thus, extending the efficient synthesis from 1D systems to 3D extra-large pore zeolites presents a new challenge.

In response to this issue, we proposed the concept of a configuration adaptation method to design novel "tetrahedral rigid SDAs," which includes: (1) inhibiting strong supramolecular interactions of SDAs by replacing aromatic rings with alkyl groups, and (2) focusing on optimizing the spatial configuration and rigidity of the SDAs to construct rigid tetrahedral structures. This approach aims to minimize the intermolecular stacking of SDAs and avoid the generation of 1D supramolecular assembly chains while stabilizing the super-cage structures to create target extra-large pore zeolites.

Based on this concept, we developed a series of rigid tetrahedral quaternary phosphonium salts as SDAs and successfully created the first stable 3D extra-large pore aluminosilicate zeolite, ZEO-1.<sup>2</sup> ZEO-1 has a suitable silicon-to-aluminum ratio (Si/Al = 14.5), a fully connected framework, and excellent thermal and hydrothermal stability. It contains 21 distinct T atoms with a unit cell volume of up to 46,900 Å<sup>3</sup>, placing it among the most complex fully connected zeolites solved to date. ZEO-1 possesses an extra-large pore system of 3D 16×16×16MR channels, and three super cages with four windows of 16×16, 16×12, or 12×12 MR, two of which are larger than those of FAU/SBS and SBT, while the third is similar in size. All these characteristics make ZEO-1 one of the most stable zeolites currently available (with a temperature resistance of 1200°C), featuring a much lower framework density and an extremely high specific surface area (close to 1000 m<sup>2</sup>/g). Its 3D 16 MR pore system and high acidity sites within the pores contribute to excellent performance in heavy oil conversion and light fuel selectivity in catalytic cracking reactions, comparable to the highly optimized ultra-stable Y (USY) zeolite, showing significant industrial application potential.

## DISCOVERY AND EXPANSION OF 1D TO 3D TOPOLOGICAL CONDENSATION MECHANISM

The extension of the new mechanism based on the topological condensation method has also proven to be an effective way to synthesize new extra-large pore zeolites. Numerous successful examples exist of 2D layers being transformed into 3D zeolites through topological condensation, but there have been no previous reports on the direct acquisition of 3D structures from one-dimensional (1D) precursor topological condensation.<sup>1</sup> Recently, we discovered a new mechanism of 1D to 3D topological condensation in zeolite synthesis, described as a "click reaction" in zeolite synthesis. Using this mechanism, we successfully synthesized two stable 3D extra-large pore zeolites, ZEO-3 and ZEO-5 as shown in Figure 1, continuously breaking through the minimum density limit of silica crystal materials.<sup>3,4</sup>

Based on the design concept of "tetrahedral rigid SDAs", a chain silicate ZEO-2 was synthesized, which was surrounded by many single four-membered rings (*s4rs*), each containing four independent silicon hydroxyl groups. Strong hydrogen bonding interactions between the *s4rs* of neighboring chains support the framework structure of ZEO-2. During the calcination process, adjacent silicon hydroxyl groups of *s4rs* undergo topological condensation, forming a *d4r* unit and resulting in the formation of a fully connected, stable 3D extra-large pore zeolite, ZEO-3. ZEO-3 features a 3D 16×14×14 MR pore system and, during the reporting period, was the silicon dioxide crystal material with the lowest known density. The unique 3D extra-large pore structure of ZEO-3 endows it with excellent volatile organic compounds (VOCs) adsorption treatment and macromolecular catalytic conversion performance.<sup>3</sup>

Furthermore, we have developed an inter-chain extension method that can further expand this new 1D to 3D topological condensation mechanism by inserting silicon between chains to enlarge the pore openings of extra-large pore zeolite up to 20 MR.<sup>4</sup> By using different silylating agents, we can insert four new silicon atoms into the *s4rs* of ZEO-2. Through topological condensation, we obtained the stable 3D extra-large pore zeolite ZEO-5, which has a 3D 20×16×16 MR pore system and a framework density of only 11.07 T/nm<sup>3</sup>, making it the most open fully connected pure silicon zeolite known to date. Its BET specific surface area reaches 1500 m<sup>2</sup>/g, and the theoretical density is only 1.10 g/cm<sup>3</sup>, very close to that of water. Titanium-doped ZEO-5 exhibits excellent catalytic performance in macromolecular oxidation. Addi-

tionally, the presence of triple four-membered ring (*t4r*) units with high tension in the ZEO-5 crystal structure breaks through the limits of traditional zeolite crystallization theory and challenges the inherent understanding of zeolite hydrothermal synthesis. This suggests that stable 3D extra-large pore zeolite structures, difficult to obtain through traditional hydrothermal synthesis, can be efficiently achieved by this new 1D to 3D topological condensation mechanism.

## CONCLUSION AND PERSPECTIVE

Over the past few decades, zeolite catalysis has driven a series of milestone technological revolutions in fields such as energy, chemical industry, and environmental science. Stable 3D extra-large pore zeolites are a novel development that has emerged from scratch. Their successful creation has enabled macromolecular selective catalysis in areas like petrochemicals, biomass conversion, and fine chemicals, presenting significant potential for catalytic transformation. However, the number of such materials remains extremely limited. The design of new template agents, particularly tetrahedral template agents based on tricyclohexyl phosphorus ends, holds great potential for this field and provides numerous possibilities. Additionally, the development of new phases based on 1D to 3D topological condensation mechanisms and the development of modular assembly methods based on 1D chains for synthesizing new extra-large pore zeolites also have great application prospects. The rational design and directed synthesis of stable 3D extra-large pore zeolites, along with the exploration of their catalytic applications in macromolecular systems, present important opportunities for advancing zeolite science.

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## AUTHOR CONTRIBUTIONS

N.Z.J., and C.F.J. wrote the paper. All authors contributed to the subsequent editing and improvement of the manuscript.

## DECLARATION OF INTERESTS

The authors declare no competing interests.