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Inorganic Chemistry

Zeolites Made to Order

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Rational zeolite synthesis has been a particularly tough nut to crack. Hypothetical zeolite structure databases have been around since the 1980s; [these structures now number in the millions](#), but only a few hundred have been synthesized.

Recently, several research groups have taken some of the trial-and-error out of transforming hypothetical structures into real materials. Writer Simon Hadlington refers to these as "[bespoke zeolites](#)."

Stretching the framework

Suk Bong Hong at the Pohang University of Science and Technology (Korea), Paul A. Wright at the University of St. Andrews (UK), Xiaodong Zou at Stockholm University, and colleagues produced two new materials by expanding the framework of a known material, the CO₂-adsorbing zeolite ZSM-25.

ZSM-25 was first made in 1981, but its structure was not known until this research team solved it last year. They found that it is an "embedded isorecticular" analogue of the known zeolite paulingite. By using theoretical studies to find the underlying "structural coding", they produced other expanded versions of the paulingite framework.

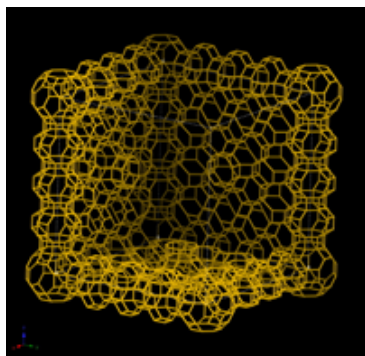


Figure 1

All of these structures are isorecticular; they share the same periodic structural topology. The expanded frameworks, however, are filled with additional cage-like structural elements that form rigid, fully connected networks. These embedded cages have similar volumes to the cages in the parent structure, so every structure in the series has the same range of pore sizes; and they are all good CO₂ adsorbents.



Figure 2

Until now, ZSM-25 had the largest known zeolite unit cell, $91.6 \times 10^3 \text{ \AA}^3$. The new zeolites, which the authors call PST-20 and PST-25, have unit cell volumes of $167.0 \times 10^3 \text{ \AA}^3$ and $275.2 \times 10^3 \text{ \AA}^3$, respectively. (*Nature* DOI: [10.1038/nature14575](https://doi.org/10.1038/nature14575))

This March, the same group published their prediction and synthesis of the next two members of this series, PST-26 and PST-28, with unit cell volumes of $422.7 \times 10^3 \text{ \AA}^3$ and $614.9 \times 10^3 \text{ \AA}^3$, respectively. (*Angew. Chem., Int. Ed.* DOI: [10.1002/anie.201510726](https://doi.org/10.1002/anie.201510726))

ZSM-25 is the type material for [framework type MWF](#) (see Figure 1). An image of [paulingite](#) is shown in Figure 2.

Zeolite Basics

More than 200 zeolite structures exist in the real world, but only about 20 of them are used in commercial applications. The emerging emissions control industry uses tens of billions of dollars' worth of zeolites; the more mature petrochemical industry uses well in excess of 100 billion dollars' worth.

Linguistic purists refer to these materials as “microporous solids”; they reserve the term “zeolite” for naturally occurring open-framework solids made from silica, alumina, and a wide variety of minor components. For convenience, we include synthetic inorganic microporous solids in the term “zeolite” here.

Likewise, many zeolite experts prefer the term “structure-directing agent” to the term “template” because the former does not imply a particular mechanism by which the inorganic crystalline framework forms around small organic molecules. These two terms are used interchangeably here.

Prefab modular units

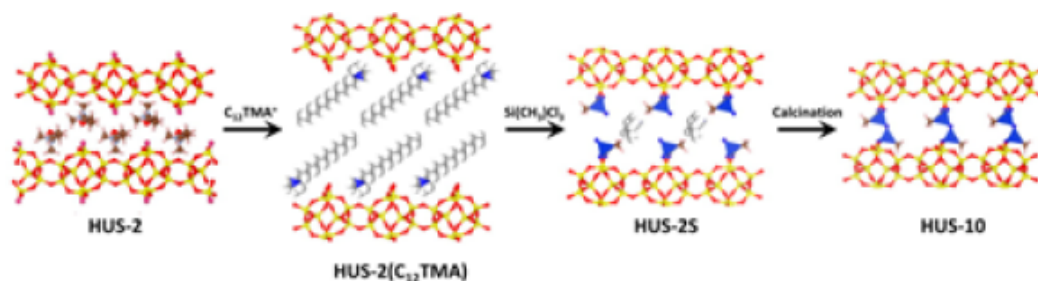


Figure 3

Nao Tsujoni, Tsuneji Sano, and colleagues at Hiroshima University (Japan), Japan Fine Ceramics Center (Nagoya), and Gifu University (Japan) found a different way to design a CO₂-adsorbing zeolite. They started with a silicate structural precursor (HUS-2; see Figure 3) that has layers covered with reactive silanol groups. Introducing trichloromethylsilane pillars between the layers and calcining the material to bond the pillars to the silanol groups form a continuous zeolite framework structure (HUS-10).

The researchers formed denser structures by bonding silanol groups from adjacent layers without intervening pillars. (*ACS Appl. Mater. Interfaces* DOI: [10.1021/acsami.5b07996](https://doi.org/10.1021/acsami.5b07996))

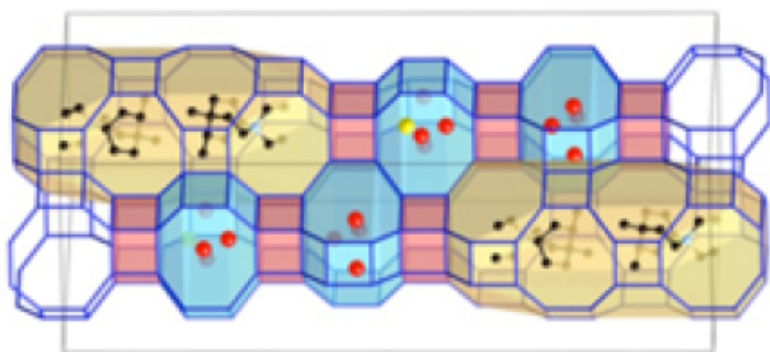


Figure 4

Growing the template to fit the space

Tracy M. Davis at Chevron Energy Technology (Richmond, CA), Michael W. Deem at Rice University (Houston), and colleagues simplified a costly synthesis of the commercially promising zeolite SSZ-52. This zeolite can catalytically reduce NO_x species in engine exhaust or convert methanol to light olefins. Figure 4 shows that this zeolite, which has framework code SFW, has a longer cage than similar commercial zeolites.

The authors compared two computational methods to identify three inexpensive, easily synthesized templates, starting with commercially available compounds and well-understood chemical reactions. In their first method, they ranked the stabilization energy of 550 known quaternary nitrogen compounds inside the SSZ-52 framework and then selected 10 compounds for experimental validation studies. Two cations promoted the crystallization of SSZ-52: *N*-ethyl-*N*-(2,4,4-trimethylcyclopentyl)pyrrolidinium (**1** in Figure 5) and *N*-ethyl-*N*-(3,3,5-trimethylcyclohexyl)pyrrolidinium (**2**).

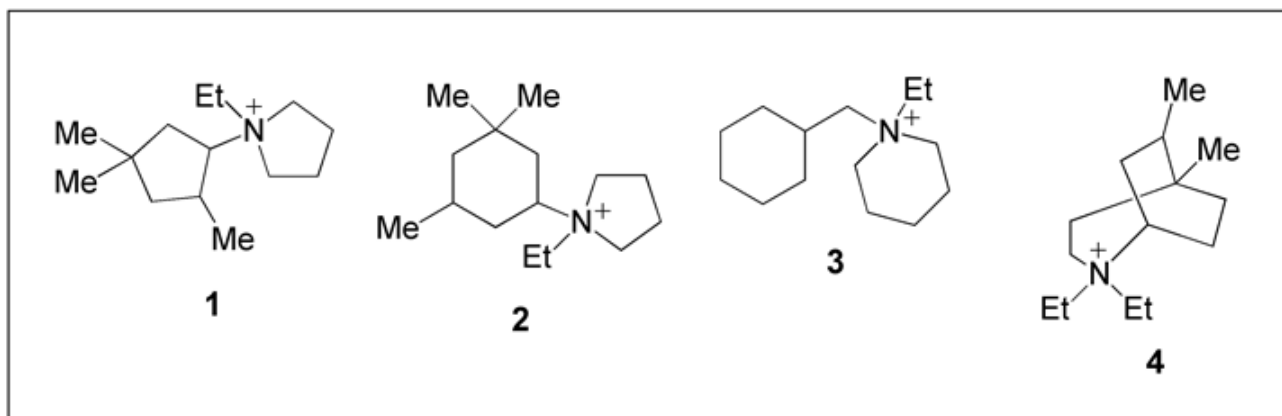


Figure 5

The second strategy used a genetic algorithm to sort through a database of $\approx 56,000$ commercially available compounds. Starting with the most promising results, the authors computationally “grew” the structure-directing agents to fit the inside of the SSZ-52 framework.

One of the resulting cations, *N*-cyclohexylmethyl-*N*-ethylpiperidinium (**3**), produced a mixture of crystalline phases in the laboratory. The mixture was formed because two molecules were not quite enough to fill the largest SSZ-52 cage, but there was not enough room for three molecules. When this compound was mixed with the more expensive original template (**4**), however, the result was pure SSZ-52. Thus, a less-than-ideal template can be mixed with a more expensive one to produce satisfactory results at a lower cost. (*Chem. Mater.* DOI: [10.1021/acs.chemmater.5b04578](https://doi.org/10.1021/acs.chemmater.5b04578))

Into the unknown

Until recently, attempts to produce bespoke zeolites involve modifying known materials or producing structural analogues, methods that have been used for decades. But advances in computational modeling and in silico synthesis, coupled with advanced lab analyses of zeolite formation mechanisms, promise to narrow the gap between the hypothetical and the actual.

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