Solving the zeolite conundrum: Researchers make 'unfeasible' zeolites

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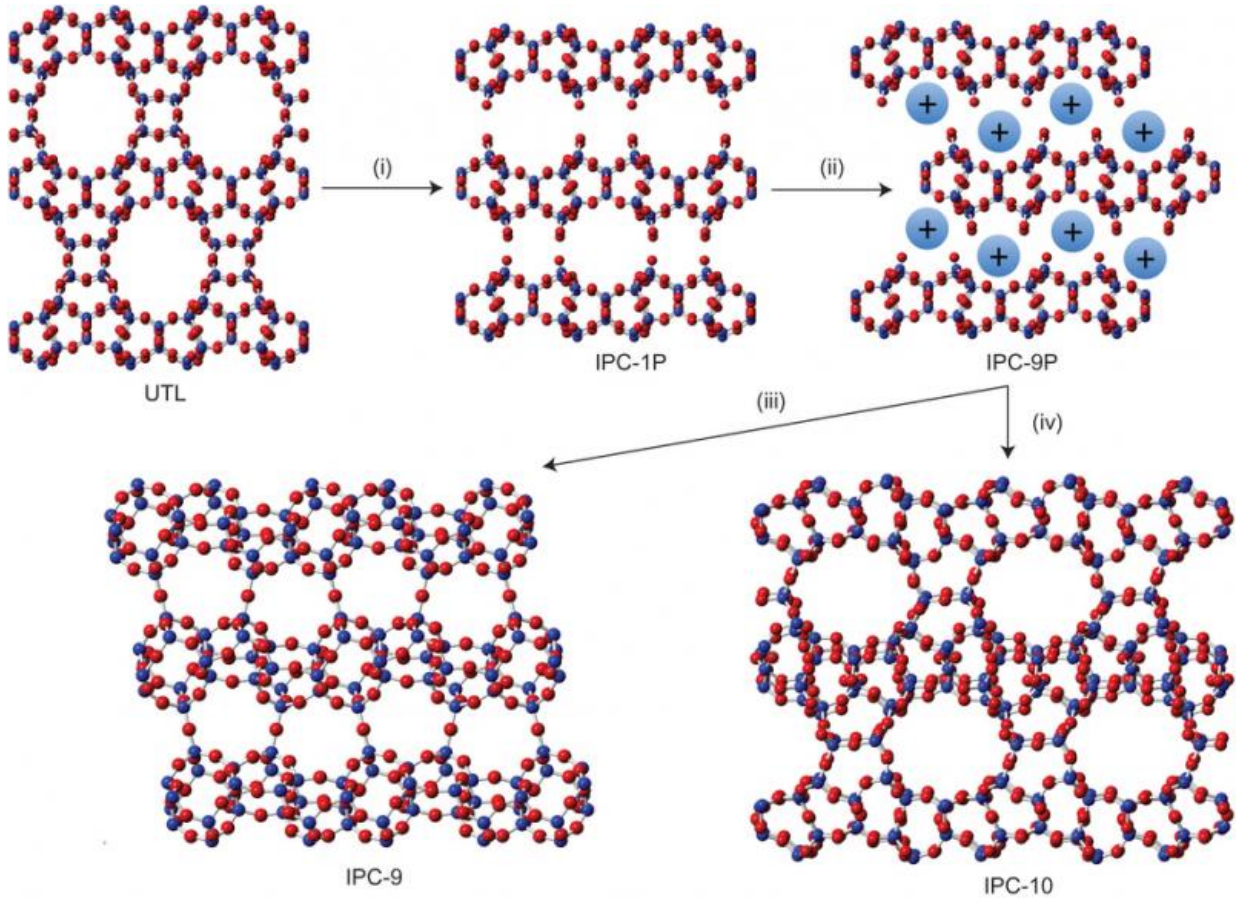

Synthesis of 'unfeasible' zeolites. The ADOR process involves the selective disassembly of a germanosilicate with, in this particular case, the UTL structure to form a layered material (called IPC-1P) (i) followed by the use of the choline cation (shown as a blue circle with a positive charge) as the SDA to shift the layers with respect to each other (IPC-9P) (ii). The layers can then be reassembled in two ways, by calcination to form IPC-9 (iii) and by calcination

after intercalation of diethoxydimethylsilane to form IPC-10 (iv). Blue, tetrahedrally coordinated silicon or germanium atoms; red, oxygen atoms. Credit: (c) 2015 *Nature Chemistry* (2015). DOI: 10.1038/nchem.2374

(Phys.org)—Zeolites, silica-based compounds known for their high surface area, have many commercial applications as absorbents and in catalysis. Since the function of the zeolite is related to its architecture, new zeolites mean the possibility of new applications. Theoretical calculations predict millions of possible zeolites, yet only about two hundred zeolites have been isolated. This oddity has been dubbed the "zeolite conundrum," and assumes that certain criteria must be met in order for a theoretical zeolite to be synthetically feasible.

New research demonstrates that "unfeasible" zeolites architectures are synthetically possible by using a different strategy than traditional sol-gel hydrothermal methods. Michal Mazur, Paul S. Wheatley, Marta Navarro, Wieslaw J. Roth, Miroslav Položij, Alvaro Mayoral, Pavla Eliášová, Petr Nachtigall, Jiří Čejka, and Russell E. Morris from the Academy of Sciences of the Czech Republic, the University of St. Andrews, the Charles University in Prague, and the University of Zaragoza have demonstrated the synthesis and characterization of two unfeasible silica-based zeolites, IPC-9 and IPC-10, using an assembly-disassembly-organization-reassembly synthetic mechanism. Their work appears in the recent issue of *Nature Chemistry*.

"At a stroke, this discovery fundamentally changes the number of potentially accessible zeolite frameworks by an order of magnitude," said Dr. Russell Morris, one of the authors of the study. "This means that new topologies with new properties are, for the first time, available for scientists to realistically target."

Because all known zeolites tend to be within a certain region in the energy density plot (range of feasible zeolites), the authors assumed that the limiting factor in making unfeasible zeolites was the traditional solvothermal method. This synthesis typically involves heating silica in a basic solution for several days. Because it is a reversible process, the zeolites outside the feasible zeolite range cannot be isolated.

Mazur, et al. employed an assembly-disassembly-organization-reassembly mechanism that they had previously reported as an alternative method for making zeolites. This synthesis involved first constructing a known zeolite, breaking the zeolite along the structural layers, and then re-building it by inserting "connectors" between layers that were slightly off-set from their low energy conformation. This allows the formation zeolites with large pore sizes and more structural strain than previously isolated ones, giving zeolites with higher energies than would be expected for their density.

To make this high-energy configuration, the authors used choline cations as their structure-directing agent. The cation intercalates between the zeolite layers, holding them in place until the calcination step in which the choline is removed and the layers reassemble. Layers with an oxygen bridge form IPC-9. If additional silicon is added, then layers with a silicon bridge form IPC-10.

X-ray diffraction and TEM studies confirmed the computationally-directed structure of IPC-9 and IPC-10 and showed that both contained a 2D channel system. Importantly, when placed on an energy-density plot of all known zeolites, IPC-9 lies on the outer edge of the region of known (feasible) zeolites and IPC-10 is well outside of this region, with higher framework energy than any known zeolites of comparative framework density. The authors note that both IPC-9 and IPC-10 fail at least one of local interatomic distance criteria would have previously been viewed as "unfeasible" zeolites.

This mechanism allows for predictable and controlled formation of high-energy "unfeasible" zeolites and sheds light on the zeolite conundrum. Because the traditional way to make zeolites involves a reversible reaction, only low-energy zeolites have been feasible synthetic targets. The procedure presented here allows for the construction of zeolites that were once thought unfeasible. According to Dr. Morris, the next step in this research is "to discover how their unique properties can be utilized in catalysis, gas separation and other applications."

More information: Michal Mazur et al. Synthesis of 'unfeasible' zeolites, *Nature Chemistry* (2015). DOI: 10.1038/nchem.2374

Abstract
Zeolites are porous aluminosilicate materials that have found applications in many different technologies. However, although simulations suggest that there are millions of possible zeolite topologies, only a little over 200 zeolite frameworks of all compositions are currently known, of which about 50 are pure silica materials. This is known as the zeolite conundrum—why have so few of all the possible structures been made? Several criteria have been formulated to explain why most zeolites are unfeasible synthesis targets. Here we demonstrate the synthesis of two such 'unfeasible' zeolites, IPC-9 and IPC-10, through the assembly–disassembly–organization–reassembly mechanism. These new high-silica zeolites have rare characteristics, such as windows that comprise odd-membered rings. Their synthesis opens up the possibility of preparing other zeolites that have not been accessible by traditional solvothermal synthetic methods. We envisage that these findings may lead to a step change in the number and types of zeolites available for future applications.