

MATERIALS SCIENCE

Pore show

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The holes of mesoporous materials provide sheltered venues for many catalytic and adsorbent processes. A complex and beautiful crystalline germanate structure widens the scope of such materials.

The discovery of ordered mesoporous materials^{1,2} has had an enormous impact on materials research. Such materials have influenced work on gels, surfactants, composite materials, nanomaterials and zeolites (catalytic and adsorbent materials familiar as, for example, water-softeners). Self-organization, surface ('heterogeneous') catalysis and separation technologies have also felt their effects. Writing on page 716 of this issue, Zou *et al.*³ introduce a mesoporous germanium oxide (germanate) material possessing exciting structural properties that could spur further investigations.

Mesoporous materials are three-dimensional bonded atomic networks punctuated by regular nanoscale holes, or pores. (The name 'mesoporous' reflects the size of the holes; materials with significantly smaller pore diameters are known as microporous, those with larger pores as macroporous.) Such materials are generally formed by the action of a negatively charged (anionic) species that include multiple oxygen-containing groups — a silicate, phosphate or aluminate, for example — on a template of a self-assembled organic molecule such as a surfactant. The ionic species match up their charges with those on the surface of the template and so attach themselves to it. The resulting rigid, periodic framework remains stable even when the organic template molecules are burnt away in a process known as calcination, creating a structure possessing pore sizes of 3–500 nanometres.

Mesoporous silicates formed in this way were originally thought to be similar in structure and function to crystalline zeolites possessing smaller pores. This would point to applications in catalysis, separation and sorption technologies — species of high molecular weight could also be used, as these could enter the larger pore spaces and undergo chemical transformations there⁴. But it turns out that using self-assembled surfactant molecules as templates produces amorphous inorganic frameworks: although the structure has mesoscopic order, leading to a characteristic diffraction pattern, atomic-level periodicity in the glass-like silicate framework is lost. This amorphous pore-wall forfeits the shape-selective properties characteristic of zeolites and important for catalysis, acting instead like slightly curved amorphous silica.

This is the remarkable aspect of Zou and colleagues' material³: the germanium oxide

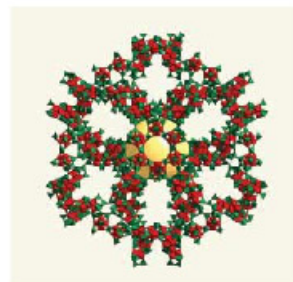


Figure 1 | Mesoporous, yet crystalline. Zou and colleagues' germanate³ combines the regular structure and shape-selectivity of a smaller-pored zeolite with larger pores useful for catalysis. (Green, [GeO₄] tetrahedra; red, [GeO₆] octahedra.)

they describe is both mesoporous and crystalline (Fig. 1). It also has the largest cell volume of any inorganic substance, with an accessible pore space that is more than 50% of the total volume. The walls of the structure's pores are formed of germanate clusters with the chemical formula Ge₁₀O₂₁(OH)₃. These are linked through Ge–O–Ge bonds and line a so-called G-minimal surface^{5,6} consisting of a complex series of concave and convex faces with cubic symmetry. (A minimal surface is one that minimizes its surface area — equivalent to its surface energy — for specified boundary conditions, rather like a film of soap in a wire frame used for blowing bubbles.) As the surface of the crystalline walls is significantly curved, the structure contains potential reactive centres that are absent in mesoporous materials lacking crystalline order. This framework fulfils the basic requirement for catalytic activity; its full scope, however, will only become apparent when the germanium sites are replaced by other metal cations.

The periodic G-minimal surface separates a set of two interpenetrating, three-dimensional channel systems that are chiral — that is, non-superimposable mirror images of each other. The interface of these two systems might form the site for stereoselective reactions that produce molecules of a particular spatial configuration. Zou and colleagues also varied³ their synthesis procedure to obtain a material that is chiral overall by blocking off one channel system with a pore filler, leaving

the other channel 'active'. Further work must show whether it is possible to obtain one pure chiral form, and whether the chiral character of the pore can be used in heterogeneous catalysis.

The mesoporous germanate is surprisingly thermally stable, its properties and structure being little affected by heat. The hydroxyl groups that become accessible in its calcined form might also be modified by ion exchange or the introduction of reactive centres into the mesoporous space, providing extra opportunities for catalysis. The smaller pore spaces in crystalline zeolites, and the instability of other ordered mesoporous materials, have until now hampered the successful application of this concept. This potential advance is indicative of a wealth of explorative lines of research using Zou and colleagues' material; time will tell whether all predictions made for its use hold.

The authors have since announced the synthesis of a further crystalline mesoporous germanate, indicating a more general chemical principle behind their findings. In their first structure, the pore geometry is similar to cubic mesoporous structures of a class known as MCM-48, which also have a periodic G-minimal surface. The second material, in contrast, has the pore topology of MCM-41-type material, with a cylindrical minimal surface arranged in a honeycomb pattern.

Zou and colleagues do not speculate on the nature of the physical or chemical mechanisms that allow germanates to yield such highly complex crystal structures. One explanation might be the structure of the Ge₁₀O₂₁(OH)₃ anion, with its core of three [GeO₄] octahedra linked along their edges, shielded by a shell of seven [GeO₄] tetrahedra linked at their corners. The highly ionic character of the octahedral bond leaves enough flexibility to link subunits, whereas the more directed bond of the tetrahedral units provides the strength and rigidity required to maintain the porous framework, even after calcination.

Unusually, therefore, it is the properties of the building blocks of the pore wall that are central to the formation of Zou and colleagues' germanates. No true templating is required from the template — just space-filling and charge-matching. It will be interesting to see what other building blocks, and which other polyoxo-metallate anions, can be used to construct further such materials.

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