

ZEOLITES

Large molecules welcome

Choosing a porous solid for catalysis usually involves a trade-off between reactivity and mass-transport properties. Polycrystalline zeolite aggregates with adjustable mesoscopic pores make both available in one material.

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Many efforts to improve the performance of heterogeneous catalysts and adsorbents focus on creating materials that are highly active and selective for their target reactants and products. This typically involves the use of porous solids with high surface areas, for instance crystalline or amorphous inorganic compounds, whose diffusional access, adsorption, and reaction properties depend strongly on their compositions and porous structures. Often, particularly in the case of large molecules or macromolecules, this means making a compromise between competing properties, such as catalytic activity versus mass-transport of reactants and products in and out of the structure. A polycrystalline zeolite, prepared by Choi *et al.* and presented on page 718 of this issue, with its high catalytic activity and mesoscopic pores (as large as 8 nm in diameter) significantly reduces the need for such compromise¹.

Zeolites are crystalline aluminosilicate materials that are technologically important for their applications in catalysis (for gasoline production), radioactive ion sequestration, purification systems (for water softening) and many more. In catalytic processes, they typically offer high activities, but their nanoporous structures (pores approximately 1 nm in diameter) rather limit their uses to reactions involving reactants and products that are small enough to diffuse in and out of nanosized pores.

A great deal of effort has been devoted to overcoming this pore-size limitation of zeolites by preparing porous inorganic solids with high surface areas and pores in the mesoscopic regime (about 2–50 nm) from gel mixtures containing zeolite 'seeds' (that is, zeolite crystals at a very early stage of nucleation). Such materials, however, have tended to have amorphous frameworks with low catalytic activities, although their pore dimensions are large enough to allow high-molecular-weight molecules to diffuse in and out of the framework structure. Where molecular order has been imparted by co-assembly with surfactant, polymeric, or carbon species to generate porosity at the mesoscale, the resulting frameworks have been composed of zeolite nanoparticles that

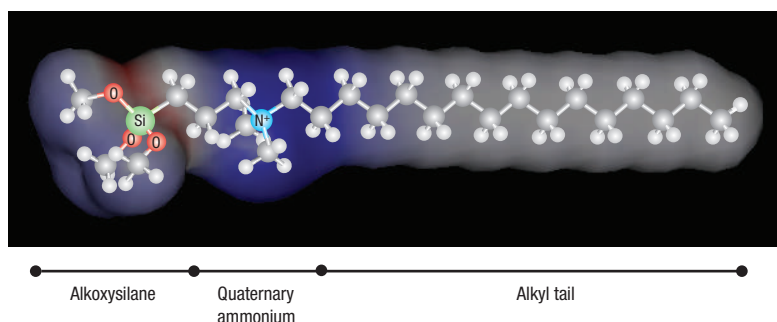


Figure 1 Multitask surfactant. The multifunctional surfactant designed by Choi and colleagues enables the synthesis of polycrystalline zeolite assemblies with relatively uniform mesopores that lead to superior performances in catalytic reactions involving large organic molecules.

displayed catalytic activity inferior to those of bulk zeolites^{2–5}, or have been thin fragile lamellae that lose their mesoporosity when calcined^{6–8}. Very recently, a more advanced strategy for controlling the aggregation of zeolite seeds, by functionalizing their exterior surfaces with organosilane species, has led to zeolite structures with bimodal nano/mesoporosities and favourable catalytic properties⁹.

An organosilane moiety is also the key to the success of Choi and colleagues' synthesis, which represents an important advance because the material obtained combines high catalytic activity with low resistances to mass-transport, and moreover offers the opportunity of tuning the size of the mesoscopic pores¹. In their synthesis, the authors combined zeolite-directing agents and meso-structure directing agents. In particular, the latter is a surfactant molecule rationally designed by Choi and colleagues to have multifunctional character (Fig. 1): a positively charged quaternary ammonium group that may facilitate zeolite-like surface structural ordering, an alkyl tail that makes the molecule amphiphilic (hydrophilic on the ammonium side and hydrophobic on the alkyl side), and an organosilane moiety linked to the ammonium group that enhances surfactant interactions with the zeolite as it crystallizes. The long alkyl tail promotes the formation of mesopores with relatively uniform size. Thus the synthesis enables hierarchical control of the dimensions of the nano- and mesopores.

X-ray diffraction analysis of the hierarchically porous product shows high angle reflections. This is new and important as it means that the structure is a single polycrystalline zeolite phase, which nevertheless retains a high degree of mesoporosity. Different zeolitic structures can, furthermore, be obtained by changing the composition of the reaction mixture and the mean size of the mesopores can be adjusted independently by changing the length of the alkyl tail or by varying the hydrothermal conditions in the reaction vessel.

Choi *et al.* then go on to demonstrate that, in catalytic reactions involving large molecules, their hierarchical nano/mesoporous zeolites are more effective than the corresponding bulk zeolites or zeolite-seed-assembled mesoporous materials. These enhanced reactivities are attributed to the combination of crystalline nanopores and uniform mesopores, although the mechanism of this enhancement is not yet established. Indeed, why nano/mesoporous zeolites show superior catalytic activities compared with polycrystalline zeolite-seed-assembled mesoporous materials is unclear, though it may depend on the mean sizes of the aggregated crystallites or their surface structures.

The authors tested one of their materials in a catalytic reaction for gasoline production and in two other syntheses of large organic molecules used in the pharmaceutical, fragrance and agrochemical industries. Once the preparation and structures are optimized, these materials may offer new opportunities for catalytic reactions or purifications involving larger molecules. These include polymers, long-chain hydrocarbons, enzymes and other large biomolecules, metal clusters for bifunctional catalysts and more, which have so far been unsuitable for use with bulk crystalline nanoporous zeolites, whose pore dimensions are generally too small to accommodate most macromolecular species. Such hierarchical nano/mesoporous zeolites are anticipated to offer new flexibility in the design and engineering of increasingly sophisticated heterogeneous catalysts for more diverse product targets and more-stringent efficiency and environmental process requirements.

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MATERIAL WITNESS

Tyred out



In July it became illegal to dump almost any kind of vehicle tyres in landfill sites in Europe. Dumping of whole tyres has been banned since 2003; now disposal of shredded tyres is also forbidden. That is going to leave European states with an awful lot of used tyres to dispose of in other ways. What can be done with them?

This is a difficult question for the motor industry, but also raises a broader issue about the life-cycle of industrial materials. The strange thing about tyres is that there are many ways in which they could be a valuable resource, and yet somehow they end up being regarded as toxic waste. Reduced to crumbs, tyre rubber can be incorporated into soft surfacing for sports grounds and playgrounds. Added to asphalt for road surfaces, it makes the roads harder-wearing.

And rubber is of course an energy carrier: a potential fuel. Pyrolysis of tyres generates gas and oil, recovering some of the carbon that went into their making. This process can be made relatively clean — certainly more so than combustion of coal in power stations.

Alternatively, tyres can simply be burnt to create heat: they have 10% more calorific content than coal. At present, the main use of old tyres is as fuel for cement kilns. But the image of burning tyres is unappealing, and environmentalists oppose the practice, disputing the claim that it is cleaner than coal. Such concerns make it hard to secure approval for either cement-kiln firing or pyrolysis. And the emissions regulations are strict — rightly so, but reducing the economic viability. As a result, these uses tend to be capacity-limited.

Tyre retreads have a bad image too — they are seen as second-rate, whereas the truth is that they can perform very well and the environmental benefits of reuse are considerable. Such recycling is also undermined by cheap imports — why buy a secondhand tyre when a new one costs the same?

Unfortunately, other environmental concerns are going to make the problem of tyre disposal even worse. Another European ruling prohibits the use of polycyclic aromatic hydrocarbon oil components in tyre rubber because of their carcinogenicity. It's a reasonable enough precaution, given that a Swedish study in 2002 found that tyre wear on roads was responsible for a significant amount of the polycyclic aromatics detected in aquatic organisms around Stockholm. But without these ingredients, a tyre's lifetime is likely to be cut to perhaps just a quarter of its present value. That means more worn-out tyres: the current 42 million tyres discarded in the UK alone could rise to around 100 million as a consequence.

Whether Europe will avoid a used-tyre mountain remains to be seen. But the prospect of an evidently useful, energy-rich material being massively under-exploited seems to say something salutary about the notion that market economics can guarantee efficient materials use. Perhaps it's time for some incentives?

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