

Zeolite nanosystems: Imagination has no limits

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‘Zeolite nanosystems: Imagination has no limits’

The technological relevance of zeolites, the desire to improve their efficiency and the inexhaustible synthetic options to tailor their properties have triggered a permanent evolution of this superclass of materials. Two zeolite nanosystems prepared by distinct approaches reflect this and offer hope for new applications.

Javier Pérez-Ramírez

The field of zeolites has rapidly and continually evolved since the introduction of the first synthetic zeolites in the 1950s. A wave of research in the 1980s and 1990s launched the discovery of new framework structures and compositions, serving as adsorbents, ion exchangers and catalysts for the production of fuels and chemicals and for environmental protection. As of today, 204 unique zeolite framework types have been identified¹, although only a handful of them have been commercialized. But not all that glitters is gold. Have you ever experienced the chaos of driving in a large metropolis consisting only of winding and narrow streets, as in Fig. 1a? The charm and possibilities of the city can be spoiled by the heavily congested traffic. A similar situation exists in zeolites, which contain micropores of molecular dimensions (<1 nm). This unique feature, essential for traditional molecular-sieve and shape-selective applications, can be a burden. Bulky molecules face impeded access, getting stuck in pore openings or finding their passage to active centres within the microporous crystal hindered. Such constraints lead to under-use of the available zeolite volume, translating into suboptimal activity, selectivity or lifetime — the key performance indicators of any catalyst. This downside triggered research that targeted improved molecular accessibility and transport by means of wide-pore and/or hierarchically organized zeolites².

Hierarchical zeolites aim to combine the intrinsic microporosity — and associated properties such as crystallinity, thermal stability, acidity and reactivity — with an auxiliary network of interconnected meso- or macropores, or both. Rather than the tangled streets of

Fig. 1a, the structures are more like the street views shown in Fig. 1b,c. A wealth of new synthetic strategies has recently led to the emergence of a wide range of hierarchically organized zeolitic systems with exciting potential applications²⁻⁵. Now, two recent studies describe bottom-up approaches to synthesize new zeolite nanosystems of related framework types, specifically ultrasmall crystals of the EMT-type zeolite⁶ and hierarchical assemblies of mesoporous faujasite-type (FAU) nanosheets⁷.

The group led by Mintova reports in *Science*⁶ how control over the very early stages of crystallization in colloidal systems is crucial to isolate important nanosized metastable phases with high purity and yield, while avoiding the use of expensive organic templates. This is illustrated for the EMT-type zeolite, a hexagonal polytype of the cubic faujasite-type (FAU) zeolite, which features a three-dimensional large (12-membered ring) micropore system and one of the lowest zeolite framework densities. The difficulty of obtaining pure EMT, only possible through the use of a costly structure-directing agent (18-crown-6 ether) under tightly controlled synthesis conditions⁸, has hampered the wider use of this zeolite. Mintova and co-workers found the trick of ‘catching’ EMT in template-free solutions: cook the synthesis gel gently for a short time only. High temperatures or long syntheses transform the EMT structure of the first metastable crystalline product into those of the more stable cubic faujasite and of the denser sodalite. One can easily foresee the possibility of capturing other important zeolite phases by deeper inspection of the very early stages of synthesis, thus avoiding the use of organic reagents that are commonly needed to stabilize the desired phases. The achievements in this paper go one step further. Synthesis at near-ambient conditions yields tiny EMT nanocrystals (6–15 nm or 50–70 nm depending on the heating method and dwell time, with a silicon to aluminium ratio of around 1), in contrast to the micrometre-sized EMT crystals obtained by conventional template assisted crystallization. In this nanosized system (resembling the organization in Fig. 1b) reactant molecules could in

principle enter through many pore openings because of the presence of textural mesoporosity, staying in the diminutive microporous domains for a very short time.

Taking a different approach, the team led by Schwieger has engineered a hierarchically organized FAU-type zeolite X, which they report in *Angewandte Chemie International Edition*⁷. This aluminium-rich zeolite, which is a common adsorbent that is industrially synthesized without a template, had previously not been convincingly attained in hierarchical form. Grounded on a softtemplating approach conceived by Ryoo's team for other frameworks⁹, this is now a reality. Schwieger and co-workers prove that the introduction of an amphiphilic organosilane surfactant, 3-(trimethoxysilyl) propyl hexadecyl dimethyl ammonium chloride (TPHAC), in the synthesis gel leads to a house-of-cards-like arrangement of zeolite X nanosheets. The assembly displays an interconnected network of micropores (diameter of 0.74 nm), intracrystalline mesopores (7 nm) and wide macroporous interstices (200 nm) situated between the nanosheet stacks. Consequently, the external surface area of the hierarchical assembly is more than 10 times that of conventional zeolite X. Schwieger and colleagues suggest that the pore systems are ideally arranged for molecules to penetrate, react and leave, resembling a well-designed metropolis with an efficient network of motorways, streets and alleys (like in Fig. 1c). Additionally, they point out that zeolite X is the first system in which the use of TPHAC gives rise to the nanosheet-type morphology. In fact, the preparation of nanosheet assemblies of other zeolite frameworks such as MFI has required the use of surfactants containing multiple quaternary ammonium groups³. Although the contributions by Mintova *et al.*⁶ and Schwieger *et al.*⁷ have different starting points and practise opposite synthetic approaches, they share the same goal: the ability to tailor zeolite properties to yield improved materials for targeted applications. Next, the promising properties of these advanced materials should be exploited in laboratory studies primarily dealing with catalytic conversions, separations and adsorption processes. For example, the

cheap synthesis of highly accessible EMT shouts for catalytic studies in reactions governed at present by the FAU-type USY zeolite. Equivalently, obtaining a hierarchically organized X zeolite opens perspectives for its central catalytic use in emerging biomass-related conversions, as well as in applications requiring fast uptake or release of ions or molecules. Assuming outstanding results in any upcoming investigations, technical implementation remains the ultimate ambition.

For these advanced materials to see use in industry, a change in mindset is required, as one moves from grams to tonnes and from powders to shaped bodies, using economical procedures that can be retrofitted in existing zeolite manufacturing facilities. Syntheses assisted by exotic reagents and organic templates, such as the above-mentioned surfactants, constitute an excellent playground in which to explore the limits of these exciting materials. But their practical and sustainable implementation currently seems unviable, owing to limited supply, high costs and often overlooked safety concerns. On the other hand, special features discovered through prohibitively expensive routes provide new insights and sharpen our ability to design cost-effective analogues. This concept is beautifully illustrated in the work of Mintova and colleagues⁶. With these stringent drivers in mind, it is thought that smart sequences of inexpensive post-synthetic modifications applied to off-the-shelf commercial samples (a top-down approach) will become an important source of industrially relevant hierarchically structured zeolites. A recent study shows that, in principle, each zeolite can be amended to its hierarchical form by application of the right combination of acid and base treatments¹⁰, whose use has been demonstrated in large scale¹¹.

In conclusion, the long-lasting success and bright future of zeolites in academic research and industrial practice emanates from the Darwinistic nature of their design, constantly adapting to the changing environment. The widening window of synthetic and post-synthetic options offers greater control of the nanostructural organization, providing application-

specific properties. Given this versatility, we can understand why a limited number of frameworks cover the whole spectrum of current industrial applications. No family of materials has so far overshadowed the impressive combination of features inherent to zeolites, but I am sure that we are all open to surprises.

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Figure 1 | Improving access. **a**, A conventional zeolite particle, containing mostly micropores, is illustrated by the crowded streets of Damascus. **b,c**, Efficient nanostructured zeolite systems are made by mimicking the hierarchical integration of roads in a functional metropolis, such as Barcelona (**b**) or Paris (**c**). The hierarchical analogues in **b** and **c** contain an interconnected network of micropores (narrow streets) and larger meso- and macropores (broader streets). The latter enhance both the micropore accessibility and mass transfer rates within the particle. Furthermore, the smaller zeolite domains imply shorter micropores and substantially increase the number of micropore mouths. The features are highly attractive for current and emerging applications of these materials. Images taken from Google Maps: **a,b**, ©2012 Cnes/Spot Image, Digital Globe, GeoEye, Institut Cartografic de Catalunya. **c**, ©2012 Cybercity.