

# Porosity: The Hegemony of Empty Space in Functional Materials Design

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**P**orosity has far-reaching implications in the design of any functional solid. As such, the development and characterization of materials with well-defined porous structures is a vibrant area of research of undisputed technological significance, finding relevance in catalysis, microelectronics, sorption, separation, and sensors, among others. With the aim of strengthening the presence of porosity as a key driver for materials design, this special issue of *Advanced Functional Materials* is dedicated to outlining exciting recent synthetic, analytical, and performance advancements related to inorganic and hybrid porous materials. This includes, but is not exclusive to, the well-known examples of mesoporous materials, zeolites and zeotypes, metal-organic frameworks (MOFs), and porous carbons.

**A**n indispensable starting point to elucidate the origins of porosity within nanoporous solids is the knowledge of their crystalline structure. While many of these materials can be isolated as single phases, rapid crystallization often inhibits the growth of single crystals large enough for conventional structure determination by X-ray diffraction. In view of this, a feature article from Zou et al. addresses new developments in electron crystallographic techniques, which have greatly extended their scope and accessibility for the non-specialist, with specific examples for zeolites, MOFs, and ordered mesoporous materials.

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**Z**eolites stand out as the most important success story of porous materials in heterogeneous catalysis. The firm establishment of secondary meso-/macroporosity as a means to boost their performance has propelled a surge of investigations devoted to methods to prepare and characterize zeolite-based materials with optimized textural properties, which are represented in two contributions of this issue. In a comparative study, nanosized ZSM-5 zeolites prepared by alkaline and fluoride-mediated routes exhibit notable differences in their performance for the reaction of methanol to hydrocarbons (see Valtchev et al.). Pursuing a distinct goal, the other contribution develops a methodology to quantify mass transfer enhancements in hierarchical ZSM-5 zeolites obtained by the post-synthetic modification of a conventional sample (see Pérez-Ramírez et al.). Through the gravimetric study of a hydrocarbon probe molecule of similar dimensions to the zeolite micropore, the relationship between intracrystalline diffusivity and mesopore surface area is determined. More importantly, the article demonstrates that the superior transport properties of hierarchical zeolites are fully preserved upon shaping into technically relevant shape.

**O**f course, in addition to catalysis, another prime application of nanoporous materials derives from their excellent selectivity and adsorption capacity for industrially relevant molecules. Accordingly, two further articles are devoted to different aspects of membranes for gas separation purposes. One underlines the importance of crystal orientation in optimizing the separation performance of ZSM-5 membranes with mixtures of xylene isomers (see Tsapatsis et al.), revealing the flexibility of the common structure-directing agent tetrapropylammonium to control

secondary growth of the seed layer. The other contribution exemplifies the permeability and selectivity benefits of introducing metal-organic frameworks, a fledgling class of sorbent materials, into polymeric membranes for the efficient separation of carbon dioxide and methane (see Gascon et al.).

**T**he ubiquitous use of porous media as catalyst supports unquestionably demands a comprehensive understanding of the relation between pore architecture and the dispersion and stability of the supported species, which is a common theme in the other three articles of this issue. In an elegant strategy to engineer yolk-shell structures by encapsulating platinum and platinum-gold electrocatalysts in carbon-based spheres, stability losses due to sintering are prevented for thousands of degradation cycles (see Schüth et al.). The retention of a uniform particle size is nicely illustrated by identical-location transmission electron microscopy. The theme of complex morphology continues with the direct synthesis of a mesostructured cobalt-molybdenum/silica hydrotreating catalyst by spray drying (see Sanchez et al.), in which the distinct localization of the oxometallic phase leads to the formation of highly active MoS<sub>2</sub> slabs embedded in the walls of the silica matrix upon sulfidation. Finally, the very promising application of gold nanoparticles supported on a highly dispersed titanium dioxide support for the photocatalytic generation of hydrogen from ethanol is reported (see Corma et al.).

**T**o conclude these opening words, I hope that readers will share the enthusiasm for the initiative to explore the remarkable essence of porosity in every aspect of materials design, finding the articles collected fascinating and inspiring.



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