Nanoporous Materials

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A Major Advance in Characterizing Nanoporous Solids Using a Complementary Triad of Existing Techniques**

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The elucidation[1] of the nature of the recently developed and highly promising mesostructured zeolite-Y, which has been proven to be an outstanding cracking catalyst,[2] by Garcia-Martinez and co-workers looks set to be a milestone in the characterization of nanoporous materials in general and of industrially significant catalysts in particular. They have deployed a triad of complementary techniques, two of which are well-established, the other one was recently introduced. They are: 1) advanced analysis of gas adsorption isotherms using non-local density functional theory and hysteresis scanning, which is an indirect but quantitatively revealing method;[3] 2) transmission electron microscopy (TEM),[4] including high-resolution imaging and electron tomography (ET);[5] and 3) another direct method, rotation electron diffraction (RED), which rapidly explores the reciprocal lattice and thereby addresses the structural integrity and details of nanometer-size materials.[6]

To overcome the disadvantages that originate from sluggish diffusion of reactant and product molecules into and out of the interior of high-surface-area microporous zeolitic catalysts, such as that used extensively for cracking of petroleum, zeolite-Y, Garcia-Martinez et al.[2] introduced the strategy of size-tailoring the mesoporosity. This is achieved by so-called surfactant templating, a post-synthesis procedure, which results in the production of hierarchical zeolites, that is, zeolites containing not only micropores (as in the original sample), but also another pore system of mesopores (20–500 Å) or even macropores (≥ 500 Å). This results in facile ingress of reactants to and egress of products from the hierarchical, mesostructured zeolite-Y. The consequential improvements in catalytic performance are striking: Significant enhancements occur in the production of transportation fuels (such as gasoline and light cycle oil) during cracking.[1,2]

In their uniquely penetrating quantitative study of mesostructured zeolite-Y, which has already been manufactured at commercial scale and has shown outstanding refinery performance,[2] Garcia-Martinez, Zou, Thommes, et al.[1] have not only convincingly shown the dual nature of the micro- and mesoporosity (Figure 1), but have also determined the respective volumes of intracrystalline micro- and mesopores. Moreover, they can distinguish between truly accessible (open) mesopores and those that are constricted: In their particular samples, the percentages were 64% and 36%. Combining this analysis with the crystallographic elucidation by RED and direct three-dimensional imaging by ET, the picture that is obtained of the mesostructured zeolite-Y is comprehensive and quantitatively interpretable.

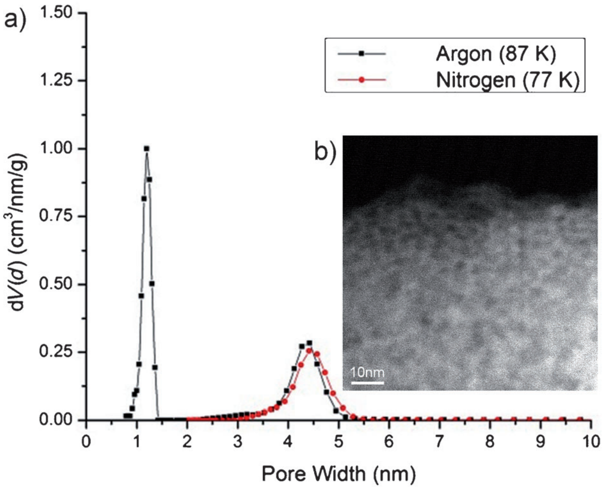

Figure 1. a) Quantitative evaluation[1] of size-tailored mesoporosity in zeolite-Y: pore size distributions illustrating the bimodal nature of the porosity, obtained by applying advanced non-local density functional theory[3] to argon and nitrogen adsorption isotherms. b) Annular dark-field scanning TEM image showing the mesopores (as dark spots).

Using high-resolution TEM (both bright-field and annular dark-field) and ET, they directly revealed the connectivity of the micro- and mesopores in the mesostructured zeolite. Furthermore, the RED approach of Zou et al.,[6] which explores the reciprocal space of a crystal under investigation, combined with ET, discloses concurrently the crystallographic

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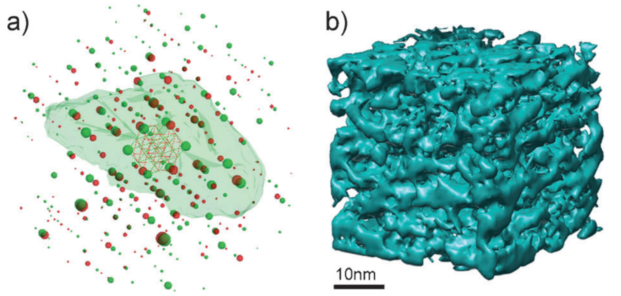

Figure 2. Rotation electron diffraction (RED) and electron tomography (ET) of mesoporous zeolite-Y.[1] a) 3D reciprocal lattices from RED, with the 3D morphology of the corresponding particle obtained from ET superimposed. This image shows that the particle is highly crystalline zeolite-Y with two twin domains (lattices shown in red and green, respectively) sharing a common [111] axis. b) A selected volume of the ET reconstruction, showing the connectivity of the mesopores.

landscape, pore architecture, and the connectivity of the mesopores, yielding the information presented in Figure 2.

This triadic approach is immediately applicable to the study of other mesostructured zeolites, such as those of practical use in industrial reactors. But what adds special interest to the paper by Garcia-Martinez, Zou, Thommes et al.[1] is that there is a vast and increasing number of inorganic, organic, and metal–organic solids and covalent organic frameworks that are potentially (and in many cases in actuality) capable of being used as adsorbents, sensors, catalysts, proton conductors and for gas storage and purification, as reported by Furukawa et al.,[7] Mitchell et al.,[8] Cooper,[9] Jones et al.,[10] and Thomas and Thomas, for example.[11] With the recent advances in preparing mesoporous metal–organic frameworks (MOFs) containing large cavities (such as the 23.3 Å pores in SUMOF-5[12]) and the development of many new catalysts consisting of multi-functionalized MOFs, the triad of techniques deployed by Garcia-Martinez, Zou, Thommes et al.[1] should prove particularly useful. The electron-beam stability of such nanoporous solids that are rich in organic moieties sometimes makes it difficult—because of electron-beam damage[4,13]—to record tilt series of micrographs required for RED and ET (recent advances in these techniques, such as strategies to reduce electron-beam exposure,[5b] may well prove helpful, and further allow robust quantitative treatment[5a,b] of the 3D structural data), but Garcia-Martinez, Zou, Thommes, and co-workers[1] have demonstrated the impressive potential scope of the combined triad of techniques.

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