Porous Materials

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Pores by Pillaring: Not Always a Maze

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Inorganic layered compounds include layered silicates such as clays, certain zeolite precursors, pervoskites, layered phosphates, and many other oxide materials. A remarkable feature of these materials is their ion-exchange capacity and the ability to form intercalates.[1] These two properties allows their structure to be modified to produce advanced multifunctional materials with unusual combinations of properties that are difficult to achieve otherwise.

Layered materials have been used as heterogeneous catalyst[2] and molecular sieve adsorbents in the past. They are currently of great interest as precursor materials for novel zeolite frameworks,[3] as exfoliated nanosheets,[4] as additives for polymer nanocomposites,[5] and as building blocks in layer-by-layer assembly to make multilayered thin films.[6,7] These materials allow tuning of optical, electronic, magnetic, and mechanical properties, and have been employed in applications such as drug delivery and corrosion protection.[8,9]

The exfoliation of layered materials to give nanometer-thick sheets is a very interesting field in itself, with numerous applications. In this Highlight we restrict our attention to the production of three-dimensionally (3D) ordered porous materials from layered materials. Examples of the formation of 3D ordered porous materials starting from layered materials can be found in some synthetic zeolite precursors. MCM-22(P)[10] and RUB-39[11] are such precursors which crystallize as layered materials and undergo topotactic condensation of the layers to produce 3D crystalline microporous frameworks upon high-temperature treatment. However, except for a few fortuitous cases like these, the fabrication of 3D ordered porous structures from layered materials has remained elusive.

The pillaring of layered materials by intercalation of suitable molecules in the interlayer space can, in principle, lead to ordered pore structures. Also, by following this approach, one can tune the interlayer pore size/shape and chemical functionality by the choice of the intercalating species. However, several challenges exist in practice. First, is the destruction of the intralayer structure during intercalation.[2,12] Figure 1 shows an example from our work where swelling of the layered silicate AMH-3 using dodecylamine results in significant changes in the intralayer bonding and introduces structural disorder into the layer structure.[12] The swelling of the layered zeolite precursor MCM-22(P) with cetyltrimethylammonium ions is another such example.[2] In some cases, the layer structure can be preserved by judiciously choosing mild swelling conditions.[13] However, to generate three-dimensional crystallinity, topotacticity or layer registry needs to be preserved. A second problem is that intercalation often results in disordered (even liquidlike[14]) placement of the intercalating species in the interlayer region and turbostratic (out of registry) arrangement of the layers (Figure 2a).

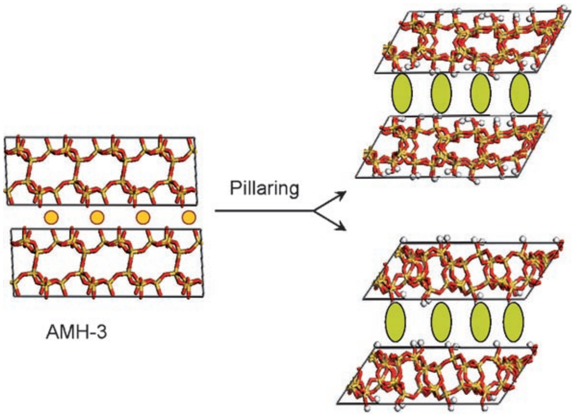

Figure 1. Changes in the intralayer structure of AMH-3 as a result of swelling with dodecylamine.[12] A mixture of at least two structures is obtained with different pore sizes and Si-O-Si bonding. Yellow: Si, red: O, green ovals: pillars.

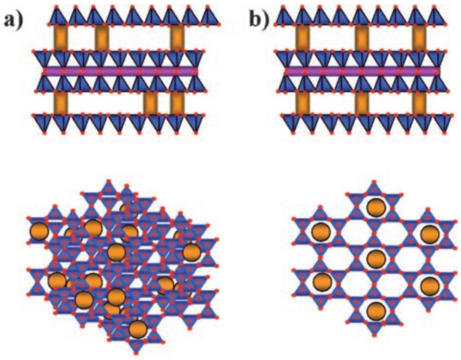

Figure 2. a) Layer materials with disordered intercalated pillars. b) 3D ordered layer material with ordered intercalated pillars and a uniform pore structure as prepared by Breu and co-workers.[16] Top: side view, bottom: top view.

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Depending on the level of disorder, structural characterization of such materials is very challenging and requires the combined use of X-ray diffraction and advanced NMR techniques.[15]

In light of the above discussion, recent work by Breu and co-workers[16] represents a leap forward in preparing 3D crystalline materials with a well-defined interlayer pore structure starting from layered materials. The authors present a microporous material obtained by oxidative pillaring of micas.[16] All the above challenges have been circumvented by a judicious choice of the starting layered material and a suitable technique to form pillars in this material. The layer structure is preserved and the pillaring process is topotactic (Figure 2b), as clearly seen from the X-ray diffraction results presented in their work. The three-dimensional crystallinity is accompanied by a well-defined pore structure in the interlayer space generated by ordered placement of the pillars. The right choice of starting material is often very important in such a self-assembly processes. The authors ensured that the precursor layered material was structurally well-ordered and had an even distribution of charge by employing crystallization from the melt rather than by solvothermal techniques. An even distribution of charge is very important as it controls the positioning of the pillars, which in turn affects the crystallographic order and the pore-size distribution. The absence of stacking faults and other structural disorder in the starting and pillared materials, together with the ability to grow large single crystals, allowed them to deduce the structure of the pillared material, including the orientation of the pillars in the interlayer spaces by single-crystal structural analysis. A knowledge of the orientation of the pillars can be important in certain applications where optically or magnetically responsive pillars are employed. Interestingly, this pillared material combines conductivity in the layers with the ordered microporosity to provide metamaterial[17] characteristics.

Their work is not limited to this particular example. In fact, they have extended the pillaring to clay hectorite by using similar techniques to obtain a microporous pillared clay.[18,19] Again, the key to success seems to be the starting material, which is free from structural defects and has a uniform distribution of charge.

One of the limitations of the materials described by Breu and co-workers is that both mica and clay layers are dense and do not provide any intralayer molecular-sieving properties nor do they allow communication between the interlayer spaces. In this respect, the ordered three-dimensional structure effectively contains 2D ordered pore spaces. Moreover, the pillaring process appears to be a collective result of weak interactions. Hence, the structural stability in the presence of strongly interacting adsorbents and/or under aggressive conditions may be compromised. The challenge to realize novel catalytically active and other metamaterials through pillaring is of course to extend the work of Breu and co-workers[16] by using other complex layered materials and pillaring molecules with reactive moieties.

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