The “Chemistree“ of Porous Solids

Mike Zaworotko

Department of Chemical Sciences and Bernal Institute, University of Limerick, Ireland

That composition and structure profoundly impact the properties of crystalline solids has provided impetus for exponential growth in the field of *crystal engineering* over the past 25 years. Crystal engineering has evolved from structure design (form) to control over bulk properties (function). Today, especially when coupled with molecular modeling and in situ characterisation, crystal engineering offers a paradigm shift from the more random, high-throughput methods that have traditionally been utilised in materials discovery and development. Simple put, custom-design of the right crystalline material for the right application, bespoke materials, is in hand.

Porous crystalline materials exemplify this situation. The “node-and-linker“ design concept has afforded more than 100,000 porous coordination networks (PCNs) since it was introduced by Robson and Hoskins in 1990. This has created a challenge for property evaluation since the number of new PCNs being produced exceeds our capacity to evaluate them properly. This is in part because whereas preliminary studies might suggest great promise for separations and/or catalysis, many PCNs are handicapped by cost or performance (e.g. poor chemical stability, interference from water vapour, low selectivity) limitations.

In this contribution, we will present an overview of the “chemistree“ (taxonomy) of porous PCNs and address why their amenability to crystal engineering is critical to enable the creation of platforms of related materials that are ideal for study of structure-function relationships. Two classes of porous materials are of particular interest:

Hybrid Ultramicroporous Materials, ***HUMs***, are built from metal or metal cluster “nodes” and combinations of organic and inorganic “linkers”. We have found that the pore chemistry and size (< 0.7 nm) of HUMs can overcome several of the weaknesses of existing classes of porous material.

Materials that switch between non-porous (closed) and porous (open) phases can exhibit isotherms that, perhaps counterintuitively, are advantangeous in terms of working capacity vs. rigid porous materials.

Specific examples of both classes of PCN will be presented and discussed in terms of their performance with respect to important gas separation (e.g. CO_2 capture, C_2H_2 capture and natural gas upgrading) and water purification applications.