

# Hybrid porous solids: past, present, future

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This critical review will be of interest to the experts in porous solids (including catalysis), but also solid state chemists and physicists. It presents the state-of-the-art on hybrid porous solids, their advantages, their new routes of synthesis, the structural concepts useful for their 'design', aiming at reaching very large pores. Their dynamic properties and the possibility of predicting their structure are described. The large tunability of the pore size leads to unprecedented properties and applications. They concern adsorption of species, storage and delivery and the physical properties of the dense phases. (323 references)

This new class of porous solids<sup>1</sup> emerged as a new domain of research ca. fifteen years ago. More or less considered at the beginning as a curiosity, it has transformed into a fully qualified field of research with an explosion of papers (Fig. 1). As usual for a new domain, most of the papers currently refer to new phases with their crystal structure and sometimes some indications about the porosity. It was a necessary step for justifying the richness of the field, as it was previously for the mesoporous compounds.<sup>2,3</sup> The latter impressed the community of zeolites and microporous phases by the huge gap in the dimensions of the pores. The interest towards hybrid porous solids concerns more the important increase in chemical versatility compared to 'classical' porous solids. The present contribution on hybrid solids will therefore be placed in the continuum of the story of porous solids, with their similarities with the other families, their advantages, their potentialities and the unprecedented properties they sometimes exhibit. It represents a global introduction to the domain of hybrid porous solids, not a complete review. Some of them have

already been recently published: for a detailed inventory of what exists see ref. 4–12.

## 1. Some definitions

Hybrid porous solids result from the reaction between organic and inorganic species in order to build up three-dimensional frameworks whose skeleton contains both organic and inorganic moieties only linked by strong bonds, at variance to supramolecular chemistry. Conceptually, there is no difference between classical inorganic porous solids and hybrid ones (Fig. 2). Indeed, the three-dimensional skeleton can be described for both of them by the association of secondary building units (SBU).<sup>13</sup> However, whereas the inorganic SBU contains only inorganic parts (tetrahedral species like SiO<sub>4</sub>, PO<sub>4</sub>, AsO<sub>4</sub>, SO<sub>4</sub>, associated with metallic cations in four-, five- or six-coordination), in the hybrid SBU, the anionic species are replaced by organic linkers, creating a contrast between the bonds within the framework: mainly covalent for the organic parts, ionocovalent for the inorganic. Moreover, as far as the porous character is concerned, organic ligands with multiple bonds must be preferred in order to ensure rigid topologies as for inorganic solids with an open framework.

The tremendous development of this family generated a new vocabulary. In the first hybrid open frameworks<sup>14–19</sup> the inorganic part contained either isolated polyhedra or small

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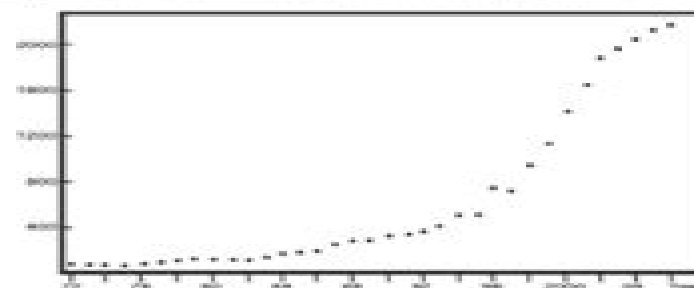


Fig. 1

# Reactivity In Solids Past Present And Future

**Michael Rajnik**



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